Effect of External and Internal Plasticization on the Glass Transition Temperature of (Meth)acrylate Polymers Studied with Molecular Dynamics Simulations and Calorimetry

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Abstract: The differences between internal and external plasticization as well as how the molecular structure of a plasticizer effects the glass transition temperature, \( T_g \), of a (meth)acrylate terpolymer is analyzed with molecular dynamics (MD) simulations and measured with differential scanning calorimetry (DSC). 1-phenoxy-2-propanol (PPH), butyl carbitol (BC) and ethylene glycol-2-ethylhexyl ether (EEH) are added either as free external plasticizers or are integrated into the polymer as internal bonded plasticizers. The simulation model is validated by finding excellent agreement of predicted \( T_g \)-values of various relevant homopolymers and terpolymers with measured values and values that are derived from established empirical equations. Simulation results suggest an aggregation of polymer alkyl groups into non-polar nano-domains. Moreover, addition of the three external plasticizers lowers \( T_g \) substantially. This \( T_g \)-loss is partially recovered after directly integrating the free plasticizers into the polymer. Bulkier plasticizers, such as BC, are more effective internal plasticizers because their larger size increase the distance between polymer chains to a larger extend, which leads to weaker average interactions among the chains, thereby reducing \( T_g \). On the other hand, more compact free plasticizers, such as PPH, exhibit a lower diffusive energy barrier that causes more frequent diffusive moves. This stimulates the diffusive movement also of the polymer, which reduces \( T_g \). Hence, integrating such a compact plasticizer into the polymer leads to a larger recovery of the \( T_g \)-loss that was induced by its free form. Overall, the complementary use of MD simulations and DSC measurements provides insights on the differences how internal and external plasticizers
influence $T_g$, respectively, and identifies the underlying molecular causes. External plasticization reduces $T_g$ more effectively than internal plasticization. Hence, a drop in $T_g$ caused by an external plasticizer can be partially recovered by integrating the plasticizer into the polymer. A possible application is the design of reactive coalescing agents for coatings that bind to the polymer after application and that could replace conventional and potentially harmful coalescing agents that evaporate into the environment.

**Keywords:** plasticizer, glass transition, MD, simulation, acrylate, dynamics

1. Introduction

Poly(meth)acrylates are used in numerous industrial and technological applications. The glass transition temperature, $T_g$, is probably the single most important descriptor of such amorphous polymers that dictates their specific application. $T_g$ is the temperature at which a transition from a glassy to a rubbery state occurs. At temperatures above $T_g$, an amorphous polymer is in a rubbery state and the polymer chains possess segmental mobility, which is beneficial for film formation\(^1\)\(^-\)\(^3\), self-healing\(^4\)\(^-\)\(^6\) properties, for energy dumping to achieve high impact polymer materials as in the case of high impact polystyrene (HIPS) and low temperature applications. The segmental dynamics and therefore the $T_g$ of a polymer is dependent on chain length, type of side chain groups, polymer sequence and presence of additives. $T_g$ is then determined by steric and electrostatic interactions among polymer groups and additives, which influence polymer chain stiffness, flexibility of side chains and distribution of additives inside the polymer matrix. Frequently, the $T_g$ of a poly(meth)acrylate can be lowered by copolymerisation with a small amount of a second monomer with high side chain flexibility, such as in butyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate or other long chain alkyl (meth)acrylates. This method is generally termed *internal plasticization* in contrast to the process of *external plasticization*, where $T_g$ is lowered by the physical addition of low molecular weight plasticizers to the parent polymer.\(^7\)\(^-\)\(^9\) The difference between the two plasticization methods is also shown in Figure 1. Internal plasticization is advantageous, considering the fact that in the case of external plasticization one needs to overcome compatibility issues of such plasticizers with the parent polymer and possible long term leaching of small volatile organic compounds (VOCs) into the atmosphere, which may affect the user over time. However, external plasticization is a more generalized approach to reduce $T_g$ and a very common approach adopted for instance for waterborne coatings for a very specific reason: In the case of waterborne latex coatings, the role of plasticizers (specifically termed in this area as coalescing agents, CAs) is to reduce $T_g$ and minimum film formation temperature (MFFT) for the latex binder. Additionally, their role is to enhance polymer diffusion
during coating drying processes, after which finally a uniform non-tacky dry coating film is obtained, once the CAs are released to the atmosphere. Nevertheless, reduction of $T_g$ via copolymerization or internal plasticization is also a common approach to synthesize latex binders with desired $T_g$. However, so far a comparison of the efficiency of these two plasticization methods mentioned earlier has not been reported in literature yet. Also, how different molecular structures of plasticizers effect changes in $T_g$ and which underlying molecular mechanisms are involved has remained unclear in large parts.

![Figure 1: External plasticization where plasticizers are free (a) and internal plasticization, where plasticizing groups are bound to the polymer (b).](image)

The effect of small molecules from gases and solvents as well as larger plasticizer compounds on $T_g$ and other properties of the glassy polymer state have been studied with MD simulations. In the pioneering work from Wagner et al. the effect of triethylcitrate on cationic polymethacrylate was studied with MD simulations to validate the applicability of this method to predict $T_g$ properties of polymers in the presence of plasticizers.\textsuperscript{10} After adding external plasticizers at different concentrations to the polymer, $T_g$-values were determined from slope changes of the simulation volume as a function of temperature, i.e. with a volumetric method. Calculated absolute $T_g$-values and plasticizer induced $T_g$-shifts were quantitatively in good agreement with DSC experiments. Also the plasticization effect of dioctyl adipate and glycidylazide oligomers on polybutadiene and polyglycidylazide has been investigated with MD simulations and compared with DSC measurements. A good quantitative agreement of absolute $T_g$-values as well as $T_g$-shifts has been observed.\textsuperscript{11} Furthermore, the plasticization effect of small compounds such as water and CO$_2$ on polymers has been studied: The reduction of $T_g$ after adding CO$_2$ at different concentrations to a polyimide membrane, as determined with the volumetric method, were in
agreement with previously measured values. The plasticization effect of water on pharmaceutically relevant hydroxypropylmethylcellulose acetate succinate and also on β-cyclodextrin has been investigated with the volumetric method. In both cases, the rate of $T_g$-reduction with increasing water concentration was predicted in agreement with measurements in the case of succinate or empirical equations, as in the case of cyclodextrin. $T_g$-values of generic polymer-solvent mixtures have also been explored with coarse-grained MD simulations, in which $T_g$ was derived from discontinuities of the polymer energy. Indeed, a linear reduction of $T_g$ with increasing solvent concentration was found. Also, the effect of generic antiplasticizers on polymers was simulated with coarse-grained MD and a decrease of $T_g$ was found, as derived from relaxation times of polymer bond autocorrelation functions. Overall, it has been demonstrated that all-atomistic MD simulations in combination with the volumetric method, the approach that was also adopted in this work, are capable of predicting quantitatively absolute values of polymer $T_g$ as well as $T_g$-shifts induced by plasticizers.

In the present work we compare the impact of external and internal plasticizers on the $T_g$ of a typical poly(meth)acrylate. Moreover, the influence of different molecular plasticizer structures on such $T_g$-shifts was explored. Two complementary methods were chosen that combine molecular dynamics (MD) simulations of poly(meth)acrylate terpolymers and differential scanning calorimetry (DSC) measurement of $T_g$ of synthesized terpolymers and terpolymer – plasticizer blends. DSC provided reliably measured plasticizer induced $T_g$-shifts, whereas MD simulations allowed us to study atomistic structures and transitions of the polymer – plasticizer systems to understand measured changes in $T_g$. The simulation model was verified in the first step by a comparison of calculated $T_g$ values of various relevant polymer systems with values that have been previously measured or that were derived from established empirical equations. After confirming the suitability of the simulation model, a typical poly(meth)acrylate was simulated with and without external and internal plasticizers, using two different plasticizers with markedly different molecular structures. Simulations were used to find polymer glass transitions. An analysis of the diffusivity of polymers and plasticizers at different temperatures allowed to formulate a relationship between diffusive barriers and $T_g$-values of the polymer. Subsequently, plasticizer induced $T_g$-shifts were measured with DSC to derive reliable values for these shifts, including also an additional third plasticizer. A combination of measured $T_g$-shifts and polymer properties derived from simulations was then used to explain the observed changes in $T_g$. Overall, differences in internal and external plasticization were analyzed to compare their effectiveness in changing $T_g$. The aim is to explore the question, whether a binding of external plasticizers to the polymer, i.e. effectively converting external to internal plasticizers, could recover the $T_g$-loss caused by external plasticization. Such an effect could be exploited for instance for the
development of reactive coalescing agents that remain inside coatings after application to replace conventional coalescing agents.

2. Simulation Methodology

2.1. Force Field
Bonded interactions in the polymer repeat units methyl methacrylate (MMA), butyl acrylate (BA), butyl methacrylate (BMA) and methacrylic acid (MAA), the plasticizers 1-phenoxy-2-propanol (PPH) and butyl carbitol (BC) as well as the corresponding internal plasticizers 1-phenoxy-2-propanol methacrylate (PPHMA) and butyl carbitol methacrylate (BCMA) were parametrized according to the force field CHARMM-36 as implemented in GROMACS 5.1. Assigned atom types are shown in Figs. S1 and S2. Atomic partial charges for all components were calculated with second order Møller-Plesset perturbation (MP2) and basis set 6-31+G(d) as implemented in the quantum chemistry software Gaussian 09. After geometry optimization, partial charges were calculated with the Merz-Kollman scheme. To capture the charge distribution of the polymer backbone, polymer units R were extended in MP2 calculations to molecules with structure CH$_3$-CH$_2$-R-CH$_2$-CH$_3$. Resulting atomic partial charges were used for non-bonded Coulomb interactions in MD simulations and are shown in Figs. S3 and S4. A standard force field with constant atomic partial charges was used instead of a polarizable force field or charge equilibration scheme to ensure a computationally affordable description.

2.2. Structure Initialization
Initial polymer structures were generated with an in-house developed Python script. The script requires atomic structures of the single units that constitute the (co)-polymer as input as well as the number of polymer chains and the degree of polymerization. The unit sequence of single polymer chains can be either explicitly defined or randomized according to specified molar ratios of the units. In our case, chain sequences were randomized individually, i.e. each chain obtained a different sequence. Polymers were initialized as stretched straight chains. Units were randomly rotated relative to the polymer backbone. Each unit was flipped relative to the backbone with a 0.5 probability to generate an atactic polymer. Chains were saturated with methyl groups at the termini. Chains were stacked in the simulation box, each randomly rotated relative to the others to minimize initial close contacts. Simulated homopolymers consisted of 4 chains with a length of 150 units each. A longer chain length of 200 units and 10 chains were used for all systems that contained terpolymers. When present, external plasticizers were added at random positions in the vicinity of the polymer chains. The resulting structures were subsequently used to initialize polymer equilibration simulations. Six replicas were generated for each simulated system. All
replicas used the same molar ratios for co-polymers, however, in order to mimic actually synthesized polymers, different individual unit sequences were used. All calculated properties presented here are averages over these replicas. An example of an equilibrated polymer system is shown in Fig. S5.

2.3. Simulation Parameters for Equilibration
All simulations were carried out using the MD simulation package GROMACS 5.1. Systems were simulated in cubic boxes with periodic boundary conditions (PBC). No degrees of freedom were constrained, except bond lengths that involved hydrogen atoms with the LINCS algorithm during the last step of the equilibration.21 Systems were simulated using isothermal-isobaric (NPT) or isothermal-isochoric (NVT) ensembles during different equilibration steps. The temperature was regulated using the velocity rescaling thermostat with a coupling constant of 0.1 ps.22 Pressure was controlled with a Berendsen barostat for increased stability of the simulations, which was necessary especially during high-pressure equilibration steps but also during heating simulations.23 The barostat coupling constant was 1 ps. Nonbonded interactions were calculated within a cut-off distance of 1.5 nm. Long range electrostatics were calculated using the fast particle-mesh Ewald (PME) method. Additionally, long-range dispersion corrections were added for van-der Waals interactions.24-26 An integration step size of 1 fs was used, except in the last equilibration step when 2 fs were used instead. Translation of the center-of-mass was corrected. Structures for analysis were written out with a frequency of 5 ps.

Generating a thermally equilibrated polymer system that is compact and exhibits a realistic density is challenging to achieve within computationally affordable simulation times. Therefore, the equilibration protocol contained a sequence of several MD steps that strived to enhance polymer mobility by using high temperatures and high pressures to ensure sufficient compactness of the system. The equilibration protocol was adapted from what was previously reported as the 21-step method.27 This protocol is characterized by simulation steps at very high temperature, in our case 1000 K, to overcome large energy barriers in the system, as well as high pressure simulations, to generate structures that are sufficiently compact. The original protocol was, however, modified because we found that in some cases experimentally determined mass densities were substantially underestimated by more than 10% with our simulation set-up. Densities derived from simulations improved to the values shown in Table 1, where also measured values are given for comparison, by extending the simulation length at the last high temperature simulation at 1000 K to 1 ns. Details of the individual equilibration steps are given in Table S1.

2.4. Method to Determine \(T_g\)
The compact equilibrated polymer system was heated up step-wise in steps of \(\Delta T = 20\) K. The system was equilibrated for 2 ns at each \(T_i\), thus yielding an effective heating rate of 10 K/ns. Therefore, for all considered systems and using six replicas in all cases, 2.2 \(\mu\)s were simulated in
Generally, heating rates used in simulations are several orders of magnitude higher than in typical DSC experiments to ensure that heating of the system across the entire temperature range can be computationally accomplished within an acceptable time. Such large heating rates are known to have a tendency to somewhat overestimate \( T_g \). For instance, according to ref. 28, an increase of the heating rate by a factor of 3000 caused an increase of a measured polystyrene \( T_g \) by 7.5 K. The specific heating rate adopted in this work, together with the used force field, provided clear glass transitions at the experimentally expected \( T_g \)-value of the homopolymer MMA, i.e. systematic errors compensated each other to reproduce measured \( T_g \)-values. It needs to be emphasized, however, that the adopted simulation protocol was adjusted only once for one system and thereafter the same simulations were applied without any changes to all simulated systems.

A heating process was preferred over cooling because of the challenges involved to generate realistic compact polymer structures, particularly at lower temperatures. A heating process enabled us to start from such a compact low temperature structure that was reliably generated with the protocol described above. Starting from a high temperature structure and subsequent cooling, however, led to substantially underestimated polymer densities once lower temperatures were reached, as revealed by a comparison with measured densities at room temperature. Cooling or heating simulations do not contain high pressure simulation steps as in the equilibration scheme above that are capable to remove excess free space in simulations. In this context it is important to note that the transition temperature observed by cooling the polymer from liquid to glassy state is called glass transition, \( T_g \), whereas heating the polymer from glassy to liquid state, as performed in this work, actually yields the fictive temperature, \( T_f \), as explained for instance in ref. 28. Even though \( T_g \) and \( T_f \) are not the same, deviations are typically small and for instance in the case of polystyrene < 1.5 K. In Figure S6 reciprocal densities and \( T_g \)-values for Poly(BA) and Poly(MMA) were compared when cooling down from a liquid to its glass state and when heating up from its glass state to a liquid. It can be observed that similar \( T_g \) values can be obtained with these two simulation methods. Considering the statistical error of at least 10 K that can be typically achieved with all-atomistic simulations of polymers this difference can be neglected and therefore \( T_f \)-values are simply referred to as \( T_g \) in the following.

To find \( T_g \) following the heating protocol, the average reciprocal mass densities, \( 1/\rho(T_i) \), at each \( T_i \) were analyzed as a function of \( T \), using the volumetric method. It is well known that \( 1/\rho(T_i) \), i.e. the volume of the system, increases linearly with constant slope until a transition occurs. After the transition, the slope adopts a larger positive value. These slopes are material constants that are closely related to the thermal expansion coefficient of the polymer. This method to determine \( T_g \) is based on the observation that the thermal expansion coefficient of a polymer changes after transition from a glassy to a rubbery state and it has been amply used in simulations due to its straightforward approach. That accurate results can be obtained with this approach
has for instance been demonstrated in ref. 29. Alternative methods include finding transition behavior of other polymer properties, such as radial distribution functions (RDF), diffusion coefficients, internal energy, thermal conductivity, Young’s modulus and others. An overview is given for instance in ref. 30.

Data points $1/\rho(T_i)$ were divided into two different groups $T < T_g$ and $T > T_g$. A straight line was fitted to each group of data points. Subsequently, $T_g$ was varied so as to minimize the error of the slope of the two regression curves. Transition points could be either between two data points $T_i$ and $T_{i+1}$, in which case $T_g$ would be simply approximated as $0.5*(T_i+T_{i+1})$ or the transition point would be at a particular data point $T_i$. Therefore, the effective resolution to determine $T_g$ was 10 K, which is sufficient considering inevitable systematic errors inherent to the simulation method. Additionally, the presence of a transition at $T_g$ was confirmed by considering also the second derivative $\partial^2 \rho(T_i)^{-1}/\partial T^2$ to detect the maximum slope change.

3. Experimental Methodology

3.1. Materials
Plasticizers BC, EEH, PPH and monomers BA, BMA, MMA, MAA (abbreviations are explained in section 2.1.), and methacryloyl chloride were received from SigmaAldrich, USA. 2,2’-Azobisisobutyronitrile (AIBN) was obtained from HalloChem Pharm Co. The monomers were passed through the basic alumina column to remove the inhibitor and were stored at -20 °C. Toluene, N,N-dimethylformamide (DMF), and dichloromethane (DCM) were purified by a Glass contour-6 solvent purification system. All other reagents were used as received.

3.2. Analysis
NMR ($^1$H, and $^{13}$C) spectra were recorded on a Bruker UltraShield Avance 400 MHz NMR instrument using deuterated solvents such as CDCl$_3$ or acetone-d$_6$ at room temperature. Molecular weight and molecular weight distribution of copolymers were measured using Waters GPC system equipped with a Waters 515 HPLC pump, 717 plus auto sampler, and 2414 refractive-index detector. The following Styragel GPC columns were arranged in a series: guard, HR5E (x2) (30 x 4.6 mm ID), HR1 and HR0.5. Tetrahydrofuran (THF) was used as an eluent with flow rate of 1 mL/min and the polymer molecular weights were calculated against narrow polystyrene standards. The mass spectrum of coalescing agent monomers was measured using the Agilent 6500 LC Q-TOF system by positive mode of ionization. $T_g$ of copolymers was measured using the Mettler Toledo DSC3 instrument at a heating/cooling rate of 10 °C/min. The DSC analysis was performed with two heating and cooling cycles and $T_g$ values were obtained from the second heating curve.
The characterization of coalescing monomers, terpolymers and terpolymer-coalescing agent blends is given in supporting information.

3.3. Synthesis and Characterization of Coalescing Monomers, Terpolymers, and Terpolymer-Coalescing Agent Blends

3.3.1. Representative Synthesis of ethylene glycol-2-ethylhexyl ether methacrylate (EEHMA)
A 50 mL two-neck round bottom flask was charged with 30 mL of dry DCM followed by ethylene glycol-2-ethylhexyl ether (EEH) (2.24 mL, 11.47 mmol) and triethylamine (2.07 mL, 14.87 mmol). The reaction mixture was cooled in an ice bath and methacryloyl chloride (1.44 mL, 14.87 mmol) was added dropwise under nitrogen atmosphere. After 18 hrs, the triethylamine hydrochloride precipitate was removed by filtration. The DCM solvent was removed using a rotary evaporator at 30 °C. The residue was dissolved in ether and washed with water three times to remove any water soluble impurities followed by drying using the rotary evaporator at 30 °C to yield 2.78 g (77 %) of off-white viscous material. The crude sample was further purified by column chromatography using a hexane/ethyl acetate solvent mixture to yield a spectroscopically pure compound. The compound structure was confirmed with 1H and 13C NMR spectroscopic analysis. The other coalescing monomers, such as BCMA and PPHMA, were synthesized with similar procedures as described in literature.31-32

3.3.2. Representative Synthesis of Poly(MMA-co-BMA-co-BCMA) (TP'(BCint)) via Solution Polymerization
In a 50 mL Schlenk tube was charged with BMA (0.84 g, 5.9 mmol), MMA (1.31 g, 13.08 mmol), BCMA (486 mg, 2.11 mmol), AIBN (26.4 mg, 1 wt%) followed by 8 mL of dry toluene and 200 µL mesitylene as internal standard. The reaction mixture was deoxygenated with three freeze-thaw cycles using nitrogen and then heated at 65 °C for 7 hrs. Samples from the reaction mixture were collected at different time and analysed with 1H-NMR to determine individual monomer conversions. Finally, the reaction mixture was diluted with small amounts of THF and the polymer was precipitated from hexane twice. Finally the polymer was dried at 50 °C for 18 hrs under vacuum to yield 2.10 g (82%).

3.3.3. Representative Preparation of TP'-PPH Blend (TP'(PPHext)) for DSC Analysis
Solutions of Poly(MMA-co-BMA-co-MAA) (TP') (500 mg in 3 mL CHCl3, [-COOH] = 4.529×10⁻³ moles) and PPH (68.92 mg in 1 mL CHCl3, 4.529×10⁻³ moles) were mixed, stirred and then transferred to a petri dish followed by drying at room temperature for 6 h (initially, for few hours, the petri dish was covered with a plastic cover that contained a small amount of CaCl₂ to avoid moisture condensation on the sample) with occasional stirring or scratching of the sample. Finally the sample was transferred to a vial and stored at -20 °C before the DSC analysis.
The characterization of coalescing monomers, terpolymers and terpolymer-coalescing agent blends is given in supporting information.

4. Results and Discussion

4.1. Validation of Simulation Model

In the first step it is crucial to validate the computation model that was used to represent polymeric systems and plasticizers as well as the simulation protocol to detect transitions in these systems. The terpolymers considered in this work consist of the following (meth)acrylic polymer repeat units commonly used to synthesize low \( T_g \) stable polymer lattices for commercial waterborne coatings: MMA, BA, BMA and MAA, see Fig. 2. Homopolymers consisting of one of these four units, respectively, were thermally equilibrated and heated as described in the Methodology. Transitions were derived from observing changes of the polymeric reciprocal mass density as a function of temperature. The results are shown in Fig. 3. Additionally, to test whether \( T_g \)-changes related to the degree of polymerization could be reproduced, short MMA homopolymers, i.e. Poly(MMA), with a polymerization degree of \( n = 20 \), instead of \( n = 150 \) that was used otherwise, were also considered. \( T_g \) was determined from \( 1/\rho(T) \) as well as its second derivative \( d^2\rho(T)/dT^2 \) as explained in the Methodology section. The obtained values of \( T_g \) were then compared with previously measured values. In case of the short \( n = 20 \) MMA homopolymer the Flory-Fox equation, \( T_g(M_n) = T_{g,\infty} - K M_n^{-1} \) was used. The \( T_g \)-value and empirical Flory-Fox parameter of Poly(MMA) has been reported as \( T_{g,\infty} = 378 \) K and \( K = 1.05 \times 10^5 \) K g/mol, respectively.\(^{33}\) With the molecular weight of Poly(MMA) for \( n = 20 \), \( T_{g,n=20} \) could be estimated as 326 K. A comparison of mass densities at room temperature and \( T_g \)-values derived from simulations with measured values is given in Table 1. An excellent agreement between simulations and experiment was obtained. At room temperature, Poly(BA) and Poly(BMA) are in their liquid state. To include also one mass density comparison of Poly(MMA) in its liquid state, densities at 390 K were added in Table 1 in parenthesis. A comparison of mass densities in the liquid state of the polymers is favorable as those states do not depend on the thermal history of the system as it is the case for polymers in their glassy state. The mass densities of Poly(MMA) at 300 K and 390 K were also compared when different heating or cooling rates were used in simulations, as shown in Table S2. Overall, mass densities vary only slightly with chosen cooling / heating rates as compared to deviations of simulation values from experiment. Mass densities at 300 K obtained with the cooling protocol were significantly lower than for the heating protocol, whereas at 390 K similar mass densities were observed.

**Table 1: Comparison of Mass Densities and \( T_g \) from Simulations with Values from Experiment and Empirical Equations**

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \rho_{\text{sim}} )</th>
<th>( \rho_{\text{exp}} )</th>
<th>( T_{g,\text{sim}} )</th>
<th>( T_{g,\text{exp/fox}} )</th>
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<tbody>
<tr>
<td></td>
<td>[g/cm(^3)]</td>
<td>[g/cm(^3)]</td>
<td>[K]</td>
<td>[K]</td>
</tr>
<tr>
<td>Material</td>
<td>Degree of Polymerization</td>
<td>Density (g/cm³)</td>
<td>Density Error (g/cm³)</td>
<td>Tg (°C)</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------</td>
<td>----------------</td>
<td>-----------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Poly(MMA)</td>
<td>150</td>
<td>1.1204</td>
<td>(1.0815)</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.15e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(MMA)</td>
<td>20</td>
<td>1.1163</td>
<td>-</td>
<td>330</td>
</tr>
<tr>
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<td>1.0173</td>
<td>1.045e</td>
<td>220</td>
</tr>
<tr>
<td>Poly(BMA)</td>
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<td>1.0271</td>
<td>1.055e</td>
<td>290</td>
</tr>
<tr>
<td>TP</td>
<td>200</td>
<td>1.1061</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>TP (55:25:20)i</td>
<td>200</td>
<td>1.1231</td>
<td>-</td>
<td>330</td>
</tr>
<tr>
<td>TP (50:20:30)i</td>
<td>200</td>
<td>1.1431</td>
<td>-</td>
<td>340</td>
</tr>
</tbody>
</table>

a  Degree of polymerization used in simulations.
b  Densities are given at room temperature.
c  Statistical uncertainties are given as subscripts.
d  Statistical uncertainty of Tg from simulations is estimated to be 10 K.
e  Measured values taken from ref. 33.
f  Derived from Flory-Fox equation.
g  Derived from Fox equation.
h  Mass densities given in parenthesis are at 390 K, i.e. above Tg.
i  The molar ratios of MMA:BA:MAA are given in parenthesis.
Figure 2: Structures of different terpolymers and terpolymer–plasticizer blends investigated with MD simulations. Abbreviations of systems used throughout manuscript are given below each structure. Plasticizers in terpolymer blends are external plasticizers, whereas plasticizers incorporated in terpolymers, replacing MAA, are internal plasticizers.
Figure 3: Reciprocal mass densities of homopolymers Poly(MMA) (a), short Poly(MMA) (b), Poly(BA) (c) and Poly(BMA) (d) are shown on the left side. The second derivatives of reciprocal mass densities with respect to temperature are shown on the right side. A chain length of \( n = 150 \) was used in all cases, except for short MMA, where \( n = 20 \) was used instead. Two linear regression curves were fitted to the reciprocal mass densities. \( T_g \) was determined by minimizing the statistical error of the two linear curves and was also confirmed by the maximum of the second derivative of the reciprocal mass.
In the next step, we simulated the terpolymer MMA-co-BA-co-MAA with a molar ratio for MMA:BA:MAA of 62:28:10, which in the following will be designated as TP. In cases where other molar ratios were used, this is specified explicitly. This molar ratio of monomers was chosen so as to achieve a glass transition near room temperature that was \textit{a-priori} estimated using the Fox equation. To test if our simulations could also reproduce changes in $T_g$ when the terpolymer composition was varied, we considered also molar ratios for MMA:BA:MAA of 55:25:20 and 50:20:30. Reciprocal mass densities of these systems as a function of temperature are shown in Fig. 4. Determined $T_g$ of these simulated terpolymers were compared with empirically estimated values using the Fox equation, $T_g^{-1} = \sum_i m_i T_{g,i}^{-1}$, with the mass fractions $m_i$ of polymer component $i$ and $T_{g,i}$ of the corresponding homopolymers. Measured values of $T_{g,i}$ for MMA, BA and MAA homopolymers have been reported as 378 K, 218 K, and 501 K, respectively,\textsuperscript{32} whereas mass fractions $m_i$ are given by the molar ratios of considered terpolymers. The full comparison is given in Table 1. Again, as in the case of the homopolymers, the predicted values for $T_g$ are in very good agreement with the values derived from the Fox equation. Overall, the root mean square (rms) deviation of simulated $T_g$ values from measured and empirically estimated values was found to be only 7.3 K. On the other hand, because heating of the polymers was carried out step-wise with temperature increments of 20 K and the fact that a transition could be observed only either between two data points or at a data point, the true statistical error cannot be smaller than 10 K. In any event, the excellent agreement of $T_g$-values shown in Table 1 indicates that the simulation model is adequate and that the simulation protocols are suitable to locate transitions reliably.

Also autocorrelation functions of the end-to-end distances of polymer chains have been determined for the systems shown in Table 1. The results are shown in Figure S7. As can be seen from these plots, autocorrelation decayed sufficiently close to zero within equilibration times for all systems.
Figure 4: Reciprocal mass densities of TP (a), TP (55:25:20) (b) and TP (50:20:30) (c) are shown on the left side. The second derivatives of reciprocal mass densities with respect to temperature are shown on the right side. Two linear regression curves were fitted to the reciprocal mass densities.

4.2. Inhomogeneity in Terpolymer
For the case of TP, structural differences in the vicinity of each of the three polymer units were investigated. The number of atoms within 0.3 nm of the center-of-mass (COM) of each polymer repeat unit type, i.e. MMA, BA or MAA, were counted and compared with the number of atoms that would have to be expected from a hypothetical homogeneous distribution of polymer unit types in the simulation system. A distance of 0.3 nm was chosen so that only atoms in direct contact with the polymer units were counted. Calculated ratios, as shown in Table 2, were defined as the number of atoms from a particular unit type actually found in simulations over the
number of atoms expected purely from stoichiometry and unit concentration of a homogeneous
distribution. For instance, the first value of 1.24 in Table 2 indicates that the number of atoms
stemming from MMA repeat units around the COM of an arbitrary MMA repeat unit in the
system increased on average by a factor of 1.24 compared to a homogenous distribution. Also, a
fourth atom group, the BA–CH₂–CH₃ butyl terminus, was introduced.

Table 2: Number of Atoms from one Repeat Unit Type in Vicinity of another Repeat Unit Type
as Derived from MD

<table>
<thead>
<tr>
<th>Vicinity of repeat unit</th>
<th>Atoms from repeat unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA</td>
</tr>
<tr>
<td>MMA</td>
<td>1.24</td>
</tr>
<tr>
<td>BA</td>
<td>0.76</td>
</tr>
<tr>
<td>MAA</td>
<td>0.84</td>
</tr>
</tbody>
</table>


Number of atoms were normalized according to their overall concentrations in terpolymer.
Repeat unit vicinity was defined as the space within 0.3 nm of any of the atoms that comprise the unit.

Most striking is an increase of atoms from BA repeat units around other BAs by a factor of 1.56.
This value increases even further to 1.72 when BA atoms only around the BA butyl terminus are
considered (not shown in Table). Also a strong increase of MAA atoms around other MAA repeat
units was observed by a factor of 1.67. To a smaller extend there is also an increase of MMA
atoms around MMA. Correspondingly, there are substantial decreases of BA atoms around MMA
and MAA repeat units. In other words, polymer repeat units of the same type tended to
aggregate to some extent, even though the sequences of polymer units in chains were
randomized. In Fig. 5 this aggregation is visualized and nano-domains composed of butyls from
BA can be clearly seen. This behavior can be explained keeping in mind that while BA repeat units
are the most hydrophobic units, MAA repeat units are the most hydrophilic, which results in an
attempt of separating these two repeat unit types as far as it is possible in a system that consists
of entangled polymer chains and randomly distributed units on these chains. The structural
constraints inside the polymer matrix naturally cause a limitation of the size of such domains.
Nevertheless, the terpolymer is inhomogeneous when viewed on a nano-scale. The observed
butyl domains contain weakly interacting alkyl chains and this suggests that only small energy
barriers would have to be overcome to enable movement of butyl chains within such domains.
Figure 5: Cross section of structure displayed in van der Waals representation taken from equilibrated TP. MMA is shown in blue, MAA in turquoise, BA without butyl in orange and butyl from BA in yellow. An aggregation of non-polar butyl chains from BA can be seen.

Generally, observing phase separation in polymer systems with atomistic simulations within typical simulation times is very challenging. However, observation of the type of inhomogeneity formation found in the present work was possible because the use of a refined multi-step equilibration protocol as described in section 2.3, which also involved phases of simulation at 1000 K to enable sufficient diffusion. Besides, aggregation of butyl chains required only limited diffusion and reorientation of sidechains considering the small size of found butyl aggregates ~ 1 nm and could therefore be accomplished within simulation times. A further aggregation of butyl chains was not observed in longer simulations.

4.3. Effect of Plasticizers on $T_g$ of Terpolymer
In simulations, two different external plasticizers were added to TP. For simulations, terpolymers containing BA were strongly preferred over terpolymers with BMA. The reason is that Poly(BMA)
exhibits a $T_g$-value at room temperature (see also Fig. 3d). Therefore, it is to be expected that the intended glass transition of the terpolymer with BMA at room temperature would broaden and therefore more difficult to determine, thereby making it difficult to determine comparably small $T_g$ changes such as those induced by plasticizers. In any case, the structures of the two added plasticizers PPH and BC are shown in Fig. 2. Henceforth, we refer to these systems as TP(PPH$_{\text{ext}}$) and TP(BC$_{\text{ext}}$) to indicate the presence of free external plasticizers. Moreover, in further simulations, the two considered external plasticizers were bound to TP at MAA repeat units as shown in Fig. 2. In these simulations, all MAA in TP were replaced with either PPHMA or BCMA. In the following, these terpolymers are designated as TP(PPH$_{\text{int}}$) and TP(BC$_{\text{int}}$) to indicate the presence of internal plasticizers. As before, $T_g$ values and other thermal transitions were determined from calculated reciprocal mass densities as functions of temperature. The results are shown in Fig. 6 and Table 3.

**Table 3: Glass transitions found with MD Simulations in Terpolymers with and without Plasticizers**

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ [K]</th>
<th>$T_s$ [K]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>TP(PPH$_{\text{ext}}$)</td>
<td>250</td>
<td>370</td>
</tr>
<tr>
<td>TP(PPH$_{\text{int}}$)</td>
<td>270</td>
<td>-</td>
</tr>
<tr>
<td>TP(BC$_{\text{ext}}$)</td>
<td>270</td>
<td>400</td>
</tr>
<tr>
<td>TP(BC$_{\text{int}}$)</td>
<td>280</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Additional high temperature slope changes of the reciprocal polymer density observed only when external plasticizers were included in the system.
Figure 6: Reciprocal mass densities of TP(PPH\text{ext}) (a), TP(PPH\text{int}) (b), TP(BC\text{ext}) (c) and TP(BC\text{int}) (d) are shown on the left side. The second derivatives of reciprocal mass densities with respect to temperature are shown on the right side. Linear regression curves fitted to reciprocal mass densities with respect to temperature are shown together with their corresponding $r^2$-coefficient. $T_g$ was determined by minimizing the statistical error of the two linear curves and was also confirmed by the maximum of the second derivative of the reciprocal mass.
We observed a decrease of $T_g$ upon addition of the free external plasticizers BC and PPH by 30 K and 50 K, respectively. When the plasticizers were bound to the polymer, in both cases $T_g$ partially recovered and increased by 10 K and 20 K in the cases of BC and PPH, respectively, when compared to their free form. This means that the external plasticizers lowered $T_g$ of the polymers as expected. It also demonstrates that a binding of the same plasticizers compromises their ability to lower $T_g$.

In Figs. 6a and 6c a second slope change of the reciprocal density could be observed at very high temperatures, which according to the second derivate occurred at 370 K and 400 K for TP(PPH<sub>ext</sub>) and TP(BC<sub>ext</sub>), respectively. Such slope changes were not observed when internal plasticizers were involved. This finding suggests that the slope changes are related to overcoming strong interactions between the free external plasticizers and the polymer, most likely electrostatic attraction between plasticizer hydroxyl groups and polymer carbonyls, i.e. the two most polar groups in these systems. As this is not the focus of the present work, we leave a confirmation and possible characterization of these slope changes for future work.

### 4.4. Diffusivity of Terpolymer and Plasticizers

To analyze the effect of plasticizers on the terpolymer further, the mean square deviations (MSD), $<\Delta r^2>$, of atoms comprising polymer segments and plasticizers, respectively, were calculated at different temperatures. Generally, the MSD of a molecular group increases with the time interval, $\Delta t$, for which the average $<\Delta r>^2$ was determined according to (in three dimensions):

$$<\Delta r^2> = 6 \cdot c \cdot \Delta t^{\alpha}$$  \hspace{1cm} (1)

In eq.1 $c$ is a time independent constant and the $\alpha$-exponent is the diffusion parameter.\textsuperscript{34}

To determine the diffusion parameters $\alpha$ encountered in simulations, log-log plots of $<(\Delta r)^2>$ as a function of the time interval $\Delta t$ were derived from some examples and are shown in Fig. S8. The diffusion parameter $\alpha$ was obtained from the slopes of these plots. Slopes between 0.17 – 0.20 were found, which indicates sub-diffusive behavior, as it is to be expected for the dynamics of polymer chains in contrast to Fickian diffusion with $\alpha = 1$. This type of diffusion results from the highly restricted movement of the entangled polymer chains.

Even though the observation of free diffusion of entangled polymer chains in atomistic simulations is not feasible within computationally accessible simulation times, the observation of single diffusive transitions of polymer segments, which are characterized by a translational motion of a polymer segment up to a few covalent bond lengths in distance per transition is possible. Together with the presence of 800 polymer units in each simulation, a sufficient number
Due to the deviation of $\alpha$ from one, (sub)-diffusion coefficients defined as $D_{\text{sub}} = \langle (\Delta r)^2 \rangle / (6\Delta t)$ are time dependent properties. This time dependency renders absolute values of $D_{\text{sub}}$ less useful when describing the dynamics of the system. However, one of the main objectives of this work is to qualitatively identify the underlying reasons for the observed performance differences of plasticizers as derived quantitatively in terms of $T_g$-shifts as discussed above. For this purpose, the property $\overline{D}_{\text{sub}}$, as defined in the following, was found to be very useful as it characterizes the diffusion of polymer segments and plasticizers, which could be compared at different temperatures and for different simulated systems relative to each other, even though its absolute value is of small relevance. Average values of $D_{\text{sub}}$ were derived for a simulation time from 0.2 – 0.6 ns from $\langle (\Delta r)^2 \rangle$, for all non-hydrogen atoms that comprised the polymer and plasticizers, respectively. This time scale was chosen to avoid the ballistic diffusive regime at smaller values of $\Delta t$ and regions of larger statistical uncertainty for larger $\Delta t$. For such a narrow range of $\Delta t$ values, $\langle (\Delta r)^2 \rangle$ increased approximately linear as shown in Fig. S9, i.e. the time dependency of $D_{\text{sub}}$ is only weak. The average sub-diffusion coefficient $\overline{D}_{\text{sub}}$ was then defined as the slope of a linear curve fitted to $\langle (\Delta r)^2 \rangle$ to yield an average diffusion coefficient for the chosen time interval. The same time-scale was chosen for all simulated systems to ensure comparability of $\overline{D}_{\text{sub}}$ across different polymer systems and temperatures to provide a measure to characterize the diffusion of polymer segments and plasticizers. The usefulness of $\overline{D}_{\text{sub}}$ will be shown in the following, as diffusive energy barriers of polymer segments derived from $\overline{D}_{\text{sub}}(T)$ were found to correlate with $T_g$.

In the next step, the temperature dependence of $\overline{D}_{\text{sub}}$ was investigated. To see whether $\overline{D}_{\text{sub}}$ follows the Arrhenius equation $\overline{D}_{\text{sub}}(T) = D_0 \exp(-E_a/RT)$, $\ln \overline{D}_{\text{sub}}$ was plotted as a function of $1/T$. as shown in Fig. 7. Indeed, $\ln \overline{D}_{\text{sub}}(T)$ exhibited linear behavior, with a change in slope at $T = T_g$, thereby confirming that the Arrhenius equation presents a reasonable approximation to describe $\overline{D}_{\text{sub}}(T)$. In the Arrhenius diffusion model, the barrier $E_a$ quantifies how much energy a diffusing compound requires to perform a diffusive transition, which is determined by the interactions of this compound with its environment. The probability for such a diffusive motion is then proportional to $\exp(-E_a/RT)$, i.e. lower barriers $E_a$ lead to more frequent diffusive movements. $D_0$ is an approximately temperature independent constant that determines how much each
individual diffusive movement contributes to \((\Delta r)^2\), i.e. it is a measure for how far on the average the diffusing molecule moves with each diffusive movement. The use of a simple Arrhenius model for diffusion provided the advantage to obtain diffusive energy barriers \(E_a\) from the slope of \(\ln \bar{D}_{\text{sub}}(T)\) that are straightforward to interpret and which provided valuable insights into \(T_g\)-shifts induced by plasticizers as shown further below.

The slope change of \(\ln \bar{D}_{\text{sub}}(T)\) at \(T_g\) is expected as the diffusive behavior of the polymer changes fundamentally at the glass transition. Accordingly, two \(E_a\)-values were derived for each system: One below \(T_g\) designated as \(E_a^\text{I}\), and one above \(T_g\) called in the following \(E_a^\text{II}\). Diffusive transitions, i.e. small movement or reorientations of polymer and plasticizer groups, were indeed also observed below \(T_g\), even though less frequently. Such transitions at low temperatures would not lead to coherent movement of large polymer parts that could give rise to macroscopic polymer movement as characteristic for a rubbery polymer state. Due to the limited length of atomistic simulations compared to polymer segment dynamics, it is not possible to directly observe the qualitative difference between diffusive transitions above \(T_g\) that lead to macroscopic polymer movement and diffusive transitions below \(T_g\) that do not. In any event, barriers were derived for TP and for TP with external and internal plasticizers. For these systems, barriers were calculated for the diffusion of polymer segments and for plasticizers, respectively. Results are shown in Fig. 7 and Table 4.

Table 4: Diffusive Barriers of Polymer Groups and Plasticizers\(^a,b\)

<table>
<thead>
<tr>
<th></th>
<th>(E_a^\text{II}) Polymer (T &lt; T_g)</th>
<th>(E_a^\text{III}) Polymer (T &gt; T_g)</th>
<th>(E_a^\text{II}) Plasticizer (T &lt; T_g)</th>
<th>(E_a^\text{III}) Plasticizer (T &gt; T_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>7.95</td>
<td>11.48</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>TP(PPH(_\text{ext}))</td>
<td>2.72</td>
<td>8.84</td>
<td>4.1</td>
<td>12.2</td>
</tr>
<tr>
<td>TP(PPH(_\text{int}))</td>
<td>4.63</td>
<td>9.1</td>
<td>5.97</td>
<td>14.2</td>
</tr>
<tr>
<td>TP(BC(_\text{ext}))</td>
<td>5.28</td>
<td>11.1</td>
<td>5.24</td>
<td>10.1</td>
</tr>
<tr>
<td>TP(BC(_\text{int}))</td>
<td>7.44</td>
<td>10.64</td>
<td>7.47</td>
<td>10.46</td>
</tr>
</tbody>
</table>

\(^a\) Statistical uncertainties are given as subscripts.  
\(^b\) \(E_a^\text{I}\) barriers were calculated for \(T < T_g\) and \(E_a^\text{II}\) for \(T > T_g\).
Figure 7: Sub-diffusion coefficients, $\ln \overline{D}_{\text{sub}}$, of polymer segments in systems TP, and TP that include external and internal plasticizers (a), as well as the diffusion coefficients of external and internal plasticizers (b).
From Fig. 7a it is clear that external plasticizers facilitated the overall diffusion, i.e. $\bar{D}_{\text{sub}}$, of the polymer as expected. Internal plasticizers, however, increased $\bar{D}_{\text{sub}}$ only slightly when compared to the original terpolymer. This behavior is expected and demonstrates that plasticizers indeed facilitated diffusion is simulations, especially when plasticizers were free. According to Fig. 7b, free plasticizers exhibited larger diffusion coefficients than the rigid polymer matrix, whereas for bonded plasticizers, their diffusion coefficients were found between those of free plasticizers and polymer segments. Interesting to note is that the barriers $E_a$ for the polymer, derived from those slopes, correlate well with previously found $T_g$-values. Lower $T_g$ values appeared to be related to lower energy barriers, as can be seen in Fig. S10. Such a relation is not surprising, as low diffusive energy barriers indicate that the movement of polymer segments is more likely, i.e. less obstructed. In other words, if the energy barrier for polymer movement is reduced, a lower temperature is sufficient to cause polymer movement, including the polymer movements that lead to a transition from a glassy to a fluid state of the polymer. A correlation of $T_g$ and $E_a^+$, however, is more difficult to recognize, which may well be due to their larger statistical error, as shown in Figure S10.

It is instructive to compare $E_a$ values across simulated systems: Generally, $E_a^+ > E_a^-$, which means that larger diffusive energy barriers are involved at $T > T_g$. This in turn indicates that bulkier molecular groups are displaced per diffusive motion, which is expected when entire polymer segments start to move at $T > T_g$. Most importantly, addition of external plasticizers reduced $E_a$-values for polymer segment movement, especially $E_a^-$, which is related to the reduction of $T_g$ caused by those plasticizers as mentioned before. In the case of $E_a^-$, diffusive energy barriers of polymer segments and plasticizers adopted similar values. This finding suggests that plasticizers and polymers at $T < T_g$ diffuse in a concerted manner. At such low temperatures, the thermal energy is only sufficient to overcome weak van der Waals interactions among non-polar alkyl groups. It is possible that the non-polar moieties of plasticizers were integrated into the non-polar nano-domains observed before, in which such diffusive motion is possible at low temperature, in contrast to strong electrostatic interactions among polar carbonyl groups that impede polymer movement in the glassy state. In other words, we observed that external plasticizers lowered the diffusive energy barriers, $E_a^-$, of non-polar groups in the glassy state of the polymer substantially, thereby making their diffusive movements more frequent, which seems strongly related to the reduction of $T_g$.

A high relevance of an availability of free space in polymer systems with respect to $T_g$ or $E_a$-barriers could be excluded. Comparing mass densities of TP with and without free plasticizers, as shown in Fig. S11, reveals that BC reduced the polymer density by 1-2 %, whereas PPH increased density by around 1 %. The ability of PPH to increase density and thereby reducing free space may be due to the compact and flat benzyl ring, which allowed more dense packing compared to
the bulkier alkyl chain of BC. Even though PPH reduced the amount of free space in the polymer system, it nevertheless reduced $E_a$ even further than BC. Therefore, it can be concluded that the availability of free space did not play a significant role in lowering $E_a$ and thus $T_g$.

According to Table 4, $E_a$-barriers of internal plasticizers bonded to the polymer were found to be larger than values for polymers with external plasticizers but also somewhat smaller than barriers of the original polymer, which also follows the trend of $T_g$. In case of $E_a^+$, similar barriers were found for polymers with free and internal plasticizers. Also, $E_a$-values of bonded plasticizers and polymer segments were found to be very similar as expected, as the internal plasticizers moved together with the polymer that they were now connected with. The increase of $E_a^-$ upon binding of the external plasticizers was caused by the loss of unconstrained plasticizer movement. Nevertheless, that $E_a^-$ still remained somewhat lower than $E_a^-$-values of the original terpolymer can be attributed to internal plasticization. Essentially, integration of external plasticizers into the polymer in our case is equivalent to a mutation of MAA units to PPHMA or BCMA. Effectively, the carboxylic acid side chains of MAA, which are very polar and responsible for strong electrostatic interactions inside the polymer, were replaced by the less polar and more weakly interacting, but also much bulkier, side chains of PPHMA or BCMA. Both, weaker interactions and more separated polymer chains due to bulkier sider chains suggest a lower $T_g$, i.e. internal plasticization, which will be discussed further in the last section 4.6.

Comparing PPH and BC plasticizers, the significantly lower $E_a$-barrier for diffusive movement of PPH is noteworthy. Compared to the compact and flat benzyl ring of PPH, the alkyl ether of BC is bulkier, i.e. the contact surface area of PPH with its neighbors is smaller than for BC. Indeed, the volumes of PPH and BC molecules are 126 cm$^3$/mol and 141 cm$^3$/mol according to the McGowan method, respectively.\textsuperscript{37} Also, the molar volumes of PPH and BC were calculated from the increase of average simulation volume after adding the free plasticizers to TP. At 300 K molar volumes of 129 cm$^3$/mol and 164 cm$^3$/mol were found for PPH and BC, respectively. Both methods clearly show the compactness of PPH relative to BC, even though PPH is only slightly lighter (152 g/mol) compared to BC (162 g/mol). In any event, at $T < T_g$ the thermal energy is only sufficient to overcome van der Waals interactions among non-polar groups. Because the strength of van der Waals interactions of a compound with its environment is proportional to their contact surface area, the $E_a^-$ barrier of PPH should be lower and thus its diffusive movement should be more frequent than that of BC. As we have already seen, the diffusive movement of non-polar polymer groups such as butyl and the plasticizer appeared to be concerted. Therefore, it is plausible that PPH was more effective at increasing the frequency of butyl chain movements than BC, i.e. $E_a^-$ for the movement of polymer segments was also found to be lower in systems that contained PPH.

A further comparison of the performance of PPH and BC plasticizers through $E_a$ barriers is difficult using simulation data only, considering also the statistical errors given in Table 4. Therefore, a
further comparison of plasticizer induced \( T_g \)-changes will be resumed after taking into account experimentally determined values.

4.5. Synthesis of Coalescing Monomers and Terpolymers

To analyse the effect of internal plasticization on \( T_g \), terpolymers, PPHMA and BCMA were synthesized, where PPH and BC compounds were covalently linked to the polymer structures as shown in Fig. 8. Another terpolymer with covalently linked EEH was also synthesized by using EEHMA. EEH contains on one hand only one bridging –O– group like PPH, but that on the other hand involves a non-polar group that is as bulky as the one in BC. Based on these characteristics and what has been discussed so far, properties of EEHMA were expected to be found between those of PPHMA and BCMA, as it remains to be seen further below.

![Figure 8: Synthesis of terpolymers from PPHMA, BCMA and EEHMA, via solution polymerization.](image)

Our attempt to synthesize TP with the same molar ratios of repeat units as it was used in simulations has been unsuccessful, however. This was caused by a lower reactivity of BA, as demonstrated by the time dependent monomer conversion during the solution terpolymerization of MMA, BA and MAA monomer combination, as illustrated in Fig. 9a. This difference in reactivity was due to the presence of acrylate and methacrylate monomers in solution. Therefore, the composition of terpolymers obtained after polymerization was different from the monomer feed. To circumvent this composition drift issue, BMA was used instead of BA to synthesize Poly(MMA-co-BMA-co-MAA) instead, which will be abbreviated in the following as TP'. The involved structures are also shown in Fig. 8. As terpolymers now contained only methacrylate units, terpolymers obtained after polymerization reactions of MMA, BMA and MAA exhibited a similar composition as the original monomer feed, as confirmed by polymerization kinetics (Figure 9b) and elemental microanalysis of Poly(MMA-co-BMA-co-MAA). The molar
composition of TP’ was MMA:BMA:MAA = 62:28:10, similar to the composition of terpolymer TP used in simulations (MMA:BA:MAA = 62:28:10), except that BMA was used instead of BA. Three other terpolymers of similar composition (MMA:BMA:RMA = 62:28:10), viz. TP’(PPH_int), TP’(EEH_int) and TP’(BC_int), as described in Fig. 8, were successfully synthesized via solution polymerization using PPHMA, BCMA and EEHMA co-monomers, respectively. All polymers were purified with at least three re-precipitation steps to avoid the presence of any unreacted monomers and were characterized by gel permeation chromatography (GPC) and elemental microanalysis. All synthesized terpolymers in this work were found to have masses $M_{n,GPC}$ ~ 20-30 kDa, similar to the mass of terpolymers used in simulations. The three terpolymers with different internal plasticizers included the same molar amount of coalescing groups. Essentially, the entire 10 mol% of MAA repeat units in TP’ were replaced by either PPHMA, BCMA or EEHMA in TP’(PPH_int), TP’(BC_int) and TP’(EEH_int), respectively. Therefore, apart from the use of BMA instead of BA, TP’(PPH_int) and TP’(BC_int) use the same composition as TP(PPH_int) and TP(BC_int) in simulations.

Figure 9: Individual monomer conversions during solution terpolymerization of MMA, BA and MAA (a), MMA, BMA and MAA (b), MMA, BMA and EEHMA (c) and an overlay of DSC plots for TP’, TP’(PPH_{ext}) and TP’(PPH_{int}).

Moreover, a physical blend of TP’ and PPH, i.e. TP’(PPH_{ext}), was produced by solution blending of TP’ with PPH using equivalent amounts of PPH and MAA in TP’, followed by air drying to remove the solvent. Therefore, this blend contained free PPH to act as an external plasticizer. Similarly,
TP'(BC_{ext}) and TP'(EEH_{ext}) blends were produced with the same method. The dried TP'-blends were analyzed with DSC to determine the effect of free external plasticizers on $T_g$ relative to TP', as shown in Fig. 9d.

### 4.6. Plasticizer Induced $T_g$-Changes in Experiment and Comparison with Simulation Results

Measured values of $T_g$ for TP' and TP' with external and internal plasticizers are summarized in Table 5. The effect of external plasticization on $T_g$ is shown in Fig. 10a. All three external plasticizers reduced $T_g$ similarly between 48 K (PPH) and 54 K (BC). Integration of the external plasticizer into the polymer, i.e. using internal plasticization, increased $T_g$ relative to external plasticization. However, in all three cases, $T_g$ still remained below $T_g$ of the terpolymer without any plasticization, TP'. We observed different recoveries of $T_g$ upon switching from external to internal plasticization systems, depending on the plasticizer used, as shown in Fig. 10b. A significantly larger recovery of 24 K was obtained with PPH than with BC (10 K) and with EEH (15 K). These $T_g$-loss recoveries essentially quantified the effect that covalently binding the external plasticizer to the terpolymer would have on $T_g$. The most effective internal plasticizer was BC, which according to Table 5 lowered $T_g$ compared to TP' by 44 K, whereas in the cases of PPH and EEH $T_g$ was lowered by 24 K and 35 K, respectively. As suspected, the additional plasticizer EEH indeed caused $T_g$-shifts between those induced by PPH and BC, as it was already expected from its molecular structure as discussed before.

**Table 5: Measured $T_g$ of TP' with External and Internal Plasticizers**

<table>
<thead>
<tr>
<th>$X$ =</th>
<th>TP'</th>
<th>TP'($X_{ext}$)</th>
<th>TP'($X_{int}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPH</td>
<td>372</td>
<td>324</td>
<td>348</td>
</tr>
<tr>
<td>BC</td>
<td>372</td>
<td>318</td>
<td>328</td>
</tr>
<tr>
<td>EEH</td>
<td>372</td>
<td>322</td>
<td>337</td>
</tr>
</tbody>
</table>

$a$ $T_g$ is given in units of K.
Figure 10: Decrease of $T_g$ of the terpolymer due to presence of external plasticizers (a) and increase of $T_g$ ($T_g$-loss recovery) upon integration of external plasticizers into the terpolymer (b). $T_g$-shifts derived from simulations involving TP are shown as red bars, whereas $T_g$-shifts derived from DSC experiments using TP' are shown as green bars. Absolute $T_g$-values are given in Tables 3 and 6.

For a comparison of measured and calculated $T_g$ values, as shown in Figure 10, only $T_g$-shifts rather than absolute values could be considered because BMA polymer units were used in synthesized TP' and not BA units as in simulated TP. Considering the small variation introduced by the additional methyl in BMA compared to the overall terpolymer, a large impact on plasticization, as quantified by $T_g$-shifts rather than absolute values, is not to be expected. In any event, a comparison of predicted and measured $T_g$-shifts as shown in Figure 10 indeed show a good agreement of trends derived from simulations with DSC data. This is especially the case when it is considered that the statistical error of calculated $T_g$-values is at least 10 K, and that BA was used in simulations instead of BMA, even though the external plasticization effect of BA on
The lowering of $T_g$ of the original terpolymer by internal plasticization is generally achieved by the fact that due to the substantially larger size of the plasticizers compared to the other side chains of the terpolymer, the average distance between polymer strands is increased. This distance increase should lead to weaker attractive electrostatic interactions among the polar carbonyl-groups of the polymer units. This effect should facilitate a sliding of polymer chains against each other and hence lower $T_g$. Because BC is more bulky than PPH and thus more effective in increasing the distance between polymer chains, BCMA units in TP(BC$_{\text{int}}$) lowered $T_g$ more than PPHMA and EEHMA in TP(PPH$_{\text{int}}$) and TP(EEH$_{\text{int}}$), respectively.

Taking into account these observations, the effect of external plasticization on $T_g$ of the original terpolymer is then a combination of two effects: (1) $T_g$ reduction due to distance increase between polymer chains, and (2) frequent external plasticizer diffusive movements transmit their movement to polymer segments through mutual electrostatic interactions. Important to note is that the size of the plasticizer translates to two opposing effects on $T_g$ in this case: The more compact shape of PPH compared to BC caused less increase in inter-polymer chain distance and is therefore less effective as an internal plasticizer. However, for the same reason, it is more effective in stimulating diffusive movement of the polymer segments and is thus more effective in recovering $T_g$ upon integration into the polymer chain. Because both effects come into play for external plasticization, PPH and BC were found to be similarly effective in lowering $T_g$.

5. Conclusion

The effect of two different plasticizers, PPH and BC, on $T_g$ of a poly(meth)acrylate terpolymer was investigated with MD simulations. These simulations were supported by DSC measurements of $T_g$-values of synthesized polymers and polymer-plasticizer blends of comparable composition. The additional plasticizer EEH was included in measurements. Of particular interest was to derive and explain changes in $T_g$ when these external plasticizers were added to the terpolymer as well as $T_g$-changes that occurred when the corresponding internal plasticizers PPHMA, BCMA and
EEHMA were directly integrated into the polymer. Adequacy of simulations were carefully verified by comparing \( T_g \)-values of relevant homopolymers and terpolymers of varying composition with measured or empirically derived values to ensure the suitability of the simulation model. An rms deviation of simulation derived \( T_g \)-values of only 7.3 K was found.

Simulations revealed inhomogeneities in terpolymers on a nano-scale caused by aggregation of non-polar butyl groups from BA and other non-polar moieties. An analysis of polymer segment diffusion provided energy barriers that quantify the energy that is required for single diffusive movements of polymer segments and plasticizers. Further analysis demonstrated that such energy barriers derived from the low temperature glassy state regime \( T < T_g \) correlated well with calculated \( T_g \)-values, where low \( T_g \)-values corresponded to low diffusive energy barriers of polymer-segments. Hence, the possibility to use these diffusive energy barriers instead of \( T_g \)-values in describing glass transitions was demonstrated. Such an approach facilitates an understanding of plasticizer induced \( T_g \)-shift as variations of \( E_a \) are more straightforward to interpret than changes in \( T_g \)-values.

A comparison of \( T_g \)-shifts induced by external and internal plasticizers derived from simulations and measured with DSC were in good agreement, thereby confirming again that the used simulation model and simulation protocols were adequate. It was measured that the three external plasticizers PPH, BC and EEH reduced \( T_g \) by similar values of 48-54 K. Integrating these external plasticizers into the polymer as internal plasticizers recovered some of this \( T_g \)-loss. A larger \( T_g \)-recovery of 24 K was achieved with PPH because of its more compact molecular structure compared to the other plasticizers. This compact structure led to weaker van der Waals interactions of PPH with its environment, which in turn led to more frequent diffusive movements of PPH and other non-polar polymer parts in the glassy state of the polymer. This stimulated diffusive motion caused a larger \( T_g \)-recovery, once PPH was bonded to the polymer in the form of PPHMA. On the other hand, BCMA was a more effective internal plasticizer because its bulkier structure caused a larger distance increase between polymer chains, which in turn led to weaker electrostatic interactions among those chains, i.e. lower \( T_g \) as compared to PPHMA. The plasticizer EEH is bulkier than PPH, however also more compact than BC, and correspondingly caused \( T_g \)-shifts that were found between those induced by the other two plasticizers.

Overall, it was shown that external plasticization was more effective to reduce \( T_g \) of a polymer than internal plasticization. Furthermore, this work also demonstrated how \( T_g \) of a polymer can be controlled by choosing suitable external and internal plasticizers. In particular, it was demonstrated that a drop in \( T_g \) caused by external plasticizers can indeed be recovered by integrating them directly into the polymer. These insights could be used for instance for the design of novel reactive coalescing agents for polymer lattices and coatings.\(^{38-43}\) Such plasticizers would reduce \( T_g \) or the minimum film formation temperature of coatings in free form, thereby boosting film formation. Moreover, when these plasticizers react with the latex binder polymer of the coating after drying, they could facilitate recovery of \( T_g \)-loss at room temperature. This could be an effective approach to prevent the release of volatile and potentially harmful coalescing agent additives from coatings to the environment.\(^{44-47}\)
Conflicts of Interest
The authors have no conflicts of interest to declare.

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