

## ARTICLE

## Effect of Anethole on the Copolymerization of Vinyl Monomers

Jean-Baptiste Lena, Alexander M. van Herk\*, Satyasankar Jana\*

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Anethole, a monomer that can be extracted from bioresources, cannot homopolymerize. Its ability to copolymerize with other vinyl monomers depends on both steric hindrance and electronic nature of the comonomer. Its copolymerization behaviour with acrylic acid, 2-ethylhexyl acrylate, styrene and methyl methacrylate was investigated. Reactivity ratios were determined with the nonlinear least square method. Even though the presence of anethole strongly retards the rate of consumption of the comonomer, its incorporation in copolymer chains can be improved with a semi batch polymerization. Finally, the side reactions that occurs during the copolymerizations – e.g. formation of branches or low molecular weight chains – were investigated. We observed that anethole not only was acting as a comonomer, but also acted as a chain transfer agent, likely due to the presence of a labile hydrogen.

## Introduction

The use of renewable biomass resources instead of traditional petrochemical raw materials is an opportunity that will contribute to a sustainable future. It has already attracted much attention<sup>1-4</sup>. Many of the opportunities are with step-growth polymers due to higher suitability of the available molecules in nature, but here we look at chain-growth polymers prepared via radical polymerization. Often radical side reactions occur with biobased monomers, like transfer to monomer. Bio-based monomers are studied extensively and could possess the same or sometimes even better performances than the traditional petroleum based materials<sup>5</sup>. Moreover, their specific structure can lead to special properties and functions that are not present in polymers made from petroleum resources (e.g. renewability, abundances, and potential chemical modifications<sup>6</sup>).

In nature, plants produce various vinyl compounds (e.g. terpenoids and phenylparanoids)<sup>7</sup>. Trans-anethole (ANE) is a derivative of  $\beta$ -methoxy styrene that can be extracted from anise, clove, cinnamon and thyme essential oil<sup>8, 9</sup> and be used as a biobased monomer directly. It has a lot of applications in food, flavour, and fragrance industries<sup>7, 10</sup>. Due to the 1,2-substituted vinyl structure leading to high steric hindrance, it cannot homopolymerize<sup>11, 12</sup>. It can however copolymerize with electron-deficient vinyl monomers<sup>6</sup>, but it usually leads to low ANE-containing copolymers, except in the case of alternating systems<sup>13</sup>. As a typical electron donor ( $e=-1.4$  in the Q-e

scheme of Alfrey-Price model), it can easily copolymerize with electron acceptors such as maleic anhydride<sup>13</sup>.

Successful cationic copolymerization of ANE with p-methoxystyrene was recently reported in the literature<sup>14</sup>. ANE has also been used as a feedstock to be transformed into a crosslinker to optimize materials for particular applications, such as high performance polymers<sup>15</sup>, thermosetting polymers with good transparency<sup>16</sup>, low dielectric material<sup>17</sup>, or a sustainable water purifier<sup>18</sup>. The use of ANE based crosslinkers usually allows improving some properties of the targeted material. For instance, it increases the glass transition temperature ( $T_g$ ).

Only a few studies of radical copolymerization of ANE are reported.

Previously, Braun *et al.* successfully carried out terpolymerizations where ANE was one of the comonomers. In some cases, systems were made of two donors and one acceptor (maleic anhydride, ANE, vinyl-iso-butylether)<sup>19</sup> and in other cases, one donor and two acceptors (ANE, maleic anhydride, fumaronitrile)<sup>20</sup> in different solvents. Final terpolymers always contained 50 mol % of acceptor and 50 mol % of donor units. Terpolymerization parameters (reactivity ratios, formation of charge transfer complexes) were studied in depth using the terminal model, the penultimate model, and charge transfer complex models. The terminal model takes into account only the last units at the radical chain end while in the penultimate model the two last units of the radical chain end are taken into account. In binary alternating systems, the penultimate model must not be used as a donor unit is always followed by an acceptor units and vice versa. In the system studied by Braun *et al.*, it is quite simplified as the three monomers cannot homopolymerize and a donor is always followed by an acceptor. In general, the terminal model suffices to accurately predict the chemical composition of the copolymers. They observed that the higher the ANE content, the higher the  $T_g$ .

The most relevant study on radical copolymerization of ANE and common vinyl monomers was carried out by Nonoyama *et al.* and published in 2014<sup>21</sup>. They copolymerized various biobased  $\beta$ -methyl

Functional Molecules & Polymers, Institute of Chemical and Engineering Sciences (ICES), Agency for Science, Technology and Research (A\*STAR)  
1, Pesek road, Jurong Island, Singapore 627 833.

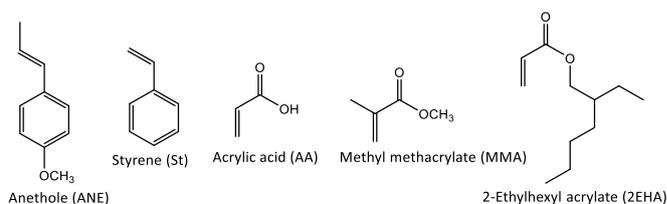
E-mail: [satyasankar\\_jana@ices.a-star.edu.sg](mailto:satyasankar_jana@ices.a-star.edu.sg) and [alexander\\_herk@ices.a-star.edu.sg](mailto:alexander_herk@ices.a-star.edu.sg)

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: More NMR spectra, kinetic data, equations and tables are presented here.

styrene (ANE, isosafrole, methyl isoeugenol, and acetyl isoeugenol) with various vinyl monomers (methyl acrylate (MA), n-butyl acrylate (nBA), t-butyl acrylate (tBA), acrylamide, and fumarate) in different solvents. Both free radical and controlled radical polymerizations were used. They showed that, (i) acrylates can copolymerize well with  $\beta$ -methyl styrene monomers and reactivity ratios were obtained with the Kelen-Tudos (KT) method; neither the bulkiness of the ester side group of the acrylate nor the polymerization temperature influenced the copolymer composition, (ii) the use of fluorinated solvent favours the incorporation of  $\beta$ -methyl styrene units in acrylate-based polymers. This is likely due to the capacity of the fluoroalcohol to coordinate with the carbonyl group. (iii) Well designed copolymers were obtained by reversible addition-fragmentation chain-transfer or RAFT polymerization. Molecular weights were controlled and a narrow molecular weight distribution was obtained ( $M_w/M_n \leq 1.2$ ), (iv) Incorporating  $\beta$ -methyl styrene units in acrylate based polymers significantly increases the  $T_g$ .

Even though Nonoyama *et al.* work was a success, we aim to push forward the previous studies by copolymerizing ANE with other vinyl-based monomers and provide a comprehensive understanding of the kinetics and mechanism of copolymerization between ANE and vinyl based monomers and investigate the potential of semi batch experiments. Acrylic acid (AA), 2-ethylhexyl acrylate (2EHA), styrene (St) and methyl methacrylate (MMA) were chosen. The structures of these monomers are presented in scheme 1. The effect of the presence of ANE on the kinetic of polymerization was investigated. Reactivity ratios were determined by the nonlinear least square (NLLS) method<sup>22</sup>. Besides the limited approaches to use acceptor-donor complexes or fluorinated solvents to help incorporation of ANE, an alternative semi batch experimental method was investigated to enhance the incorporation of ANE in vinyl based copolymers. In such experiments, a "fast" monomer (here AA, 2EHA, St and MMA), are partially fed according to a feeding profile determined from the monomer properties and reactivity ratios with the MAP software package<sup>23, 24</sup>. Semi batch processes have already been successfully applied in many other cases, such as styrene/butyl methacrylate<sup>25</sup> and butyl methacrylate/ 2-hydroxyethyl methacrylate<sup>26</sup> to obtain copolymers with precisely designed composition profile and to improve the degradability of poly(alkyl acrylates)<sup>27</sup>. Finally, we investigated the potential side reactions that occur in such copolymerization systems. We have observed that increasing ANE feed during copolymerization led to a copolymer with lower number of the average molecular weight  $M_n$ . This suggests potential transfer to the ANE monomer. Both branching and  $\beta$ -scission reactions in AA and 2EHA polymerization are affected by the presence of ANE in the system.



Scheme 1: Vinyl monomers used for this study

## Materials and methods

### Materials

Methyl methacrylate (99 %), Acrylic acid (99 %), 2-Ethylhexyl acrylate (98 %), 1,1'-Azobis (cyclohexanecarbonitrile) (ACHN) (98 %) and 1,3,5 trioxane ( $\geq 99.9$  %) were provided by Aldrich. Styrene ( $\geq 99$  %), 2,2'-Azobisobutyronitrile (AIBN) was obtained from Hallo-Chem Pharm. Co. Ltd, trans-Anethole ( $\geq 99$  %), and 1,4 dioxane anhydrous (99.8 %) were obtained from Sigma-Aldrich. (trimethylsilyl) diazomethane, 2M solution in diethylether was purchased from Acros organic. Chloroform D (D, 99.8 %) + silver foil, Dimethyl sulfoxide-D<sub>6</sub>, Methylene chloride - D<sub>2</sub> (D, 99.8 %), methanol-D<sub>4</sub> (D, 99.8 %) were obtained from Cambridge Isotope Laboratories Inc. Toluene, Methanol, Dichloromethane, Tetrahydrofuran, and dimethylformamide were purchased from WWR chemicals. Hexane was obtained from Aventor performance materials. Activated basic alumina were obtained from Alfa Aesar.

### Polymerization

MMA, 2EHA and St were purified through activated basic alumina. AA was distilled under reduced pressure. ANE, ACHN and AIBN were used as received. Batch and semi batch experiments were carried out. 2EHA, MMA, and St were homopolymerized and copolymerized with ANE either in toluene or in bulk. Toluene was used due to its high boiling point and considering the solubility of homo/copolymer produced. However, AA homopolymerization and AA/ANE copolymerization were carried out in 1,4 dioxane by considering the solubility of PAA and AA-ANE copolymers in this solvent. Experiments are summarized in table 1.

For batch polymerization, both monomers, solvent and initiator were introduced into a Schlenk flask. For styrene/ANE semi batch copolymerizations, all ANE, 4 % of the St and toluene were in the batch. 96 % of the St and the initiator were fed with a feeding pump. For 2EHA/ANE semi batch experiments, co-feeding was applied. All ANE and part of the solvent was in the batch. 2EHA and the initiator ACHN dissolved in toluene were fed separately. The proportions of toluene in the batch and fed with ACHN were chosen to maintain [Monomers] = 50 wt % to solvent in the batch. Schlenk flasks were degassed by bubbling argon through the solution for one hour. Then, flasks were placed into an oil bath at 70 °C or 90 °C or 95 °C for the reaction time.

After the intended reaction time (see Table 4), polymerizations were quenched in ice water. Poly(acrylic acid) (PAA) and poly(acrylic acid-co-anethole) (P(AA-co-ANE)) were precipitated in hexane and filtered under vacuum. Poly(methyl metacrylate) (PMMA), poly(methyl metacrylate-co-anethole) (P(MMA-co-ANE)), poly(styrene) (PSt), and poly(styrene-co-anethole) (P(St-co-ANE)) were precipitated in methanol and filtered under vacuum. Poly(2-ethylhexyl acrylate) and poly(2-ethylhexyl acrylate-co-anethole) (P(2EHA-co-ANE)) were precipitated in methanol, dissolved in dichloromethane and dried with a rotary evaporator. In the case of P(St-co-ANE), P(MMA-co-ANE), and P(2EHA-co-ANE), the precipitation was repeated twice in order to remove the ANE.

Once purified, polymers were dried overnight in a vacuum oven. Monomer conversions and copolymer compositions were determined by  $^1\text{H}$  NMR spectroscopy.

In order to measure the evolution of the monomer conversion by  $^1\text{H}$  NMR spectroscopy, 1,3,5 trioxane was added as internal standard for AA homopolymerization and AA/ANE copolymerization. For MMA, 2EHA and St homopolymerizations, dimethylformamide was added as internal standard. For MMA/ANE, 2EHA/ANE and St/ANE copolymerization, no internal standard was used. The methoxy protons of ANE as well as the protons adjacent to the oxygen in MMA and 2EHA were used as reference. Details are given in the Electronic Supplementary Information (ESI) (figures S1 and S2 as well as Equations S1 to S6).

### NMR spectroscopy

NMR spectra were recorded on a 400 MHz Bruker Ultrashield Avance 400SB Spectrometer equipped with a BPO probe and variable temperatures capabilities, operating at a Larmor frequency of 400.23 MHz for  $^1\text{H}$  and 100.65 MHz for  $^{13}\text{C}$ . Data were acquired in different deuterated solvents at 21 °C. Conversion monitoring were performed in chloroform D for St, MMA, 2EHA homopolymerization and St/ANE, MMA/ANE, 2EHA/ANE copolymerization systems and in dimethyl sulfoxide D6 for AA homopolymerization and AA/ANE copolymerization. The composition of pure copolymers was determined in methylene chloride D<sub>2</sub> for P(St-co-ANE), P(MMA-co-ANE) and P(2EHA-co-ANE) copolymers, and in methanol D<sub>4</sub> for P(AA-co-ANE) copolymers.  $^{13}\text{C}$  NMR analyses were performed in Chloroform D for P2EHA and P(2EHA-co-ANE)s, and in dimethyl sulfoxide D<sub>6</sub> for PAA and P(AA-co-ANE)s. For conversion monitoring by  $^1\text{H}$  NMR Spectroscopy, 0.1 to 0.2 mL of reactional medium were dissolved in about 0.5 mL of deuterated solvent. Analyses of final products were carried out at 50 mg.mL<sup>-1</sup> and 500 mg.mL<sup>-1</sup> for  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements respectively. One-dimensional  $^1\text{H}$  NMR spectra were acquired with 64746 data points, 32 and 128 scans for conversion monitoring and analyses of pure copolymers respectively, 29.9585 ppm spectral width (11990.407 Hz), 1 s delay, 2.70 s acquisition time and a 25 ° flip angle. One-dimensional  $^{13}\text{C}$  NMR spectra were recorded with 65536 data points, 4000 to 15700 scans, 238.2643 ppm spectral width (23980.814 Hz), 10 s relaxation delay,

1.37 s acquisition time and a 90 ° flip angle with inverse-gated decoupling. The chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

The Degree of branching (DB) and the degree of  $\beta$ -scission ( $D\beta S$ ) can be calculated by comparing the integrals of the signals of carbons that are present only when a branching event (or a beta scission event) occurs and the integral of the signal of a carbon whose characteristics remain unchanged over the polymerization process.  $DB$  on the acrylate skeleton ( $DB_{acrylate}$ , defined as the number of branches on the acrylate skeleton per acrylate monomer units) was quantified in percentage of monomer units by comparing the integral,  $I$ , of the C of a carbonyl group adjacent to a branch, which appear at 172-173 ppm and of the C of the main carbonyl group of acrylate at 174-175 ppm. As follow:

$$DB_{acrylate} (\%) = \frac{100.I(C=O)_{branches}}{I(C=O) + I(C=O)_{branches}} \quad (1)$$

The quaternary carbon at a branching point exhibit a signal at 48 ppm in branched PAA and P2EHA<sup>28, 29</sup>. However, it could not be used as it overlapped with the primary carbon linked to the aromatic ring of polymerized ANE.

The degree of  $\beta$ -scission  $D\beta S$  of P2EHA and P(2EHA-co-ANE) was also calculated in percentage of acrylate monomer units by comparing the integrals of the quaternary unsaturated carbon produced by  $\beta$ -scission at 138 ppm<sup>28</sup> and of the carbon adjacent to an oxygen atom in the ester side group at 64 ppm. We note that such terminal double bond could also be due to termination by disproportionation. However,  $\beta$ -fragmentation was almost systematically observed in poly(alkyl acrylate) formed at such high temperature<sup>28, 30-33</sup>. So we consider the effect of disproportionation negligible.

$$D\beta S_{acrylate} (\%) = \frac{100.I(C_q^{\beta-scission})}{I(C-O-R)} \quad (2)$$

The relative standard deviation ( $RSD$ ) of  $DB$  (in percent of  $DB$  values) was calculated from the signal-to-noise ratio ( $SNR$ ) of the carbon of a carbonyl group adjacent to a branch using Eq. (3), which was established for branching measurements in polyethylene by combination of a derivation from calculation error and empirical results<sup>34</sup>, and was assessed to be accurate also for branching measurements in hydrophobic polyacrylates<sup>35</sup>.

$$RSD = \frac{238}{SNR^{1.28}} \quad (3)$$

As the time between two pulses (acquisition time + delay) was the same for all  $^{13}\text{C}$  NMR analyses, the study of  $^{13}\text{C}$  NMR analyses and the Nuclear Overhauser Effect (NOE) was suppressed by using the program inverse gated decoupling, the quantifications of copolymer compositions and branching are semi quantitative.

Values of  $DB_{Acrylate}$  and  $D\beta S$  as well as examples of  $^{13}\text{C}$  NMR spectra are in ESI (figure S5 and S6 and table S19).

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**Table 1:** Details of ANE copolymerization reaction conditions with St, MMA, 2EHA and AA and copolymers produced

Reaction Code	Comonomers (mole ratio)	Process	Solvent <sup>d</sup>	Reaction time, min	Aim of experiments	Vinyl conv.	ANE conv. (%)	Overall conv. (%)	ANE fraction in the copolymer	Mn, kDa (Mw, kDa) Dispersity#	
Polymer 1	St : ANE (1 : 0)	Batch	Toluene	500	Effect of ANE on the kinetic of St polymerization, ANE incorporation to the copolymer produced and rough estimation of the reactivity ratios of St & ANE	98	-	98	-	23.3 (47.7) 2.05	
Polymer 2	St : ANE (1 : 1.5)	Batch	Toluene	1320		90	10	41	0.15	6.50 (15.7) 2.42	
Polymer 3	St : ANE (1 : 1)	Batch	Toluene	1350		81	9	44	0.10	6.90 (11.3) 1.64	
Polymer 4	St : ANE (1 : 9)	Batch	-	30	Accurate determination of reactivity ratios of St & ANE and determination of the transfer constant of Pst to ANE	16	<1	2	0.31	3.35 (4.15) 1.24	
Polymer 5	St : ANE (1 : 9)	Batch	-	30		11	1	2	0.31	3.35 (4.25) 1.27	
Polymer 6	St : ANE (1 : 9)	Batch	-	30		05	<1	1	0.29	3.70 (5.90) 1.69	
Polymer 7	St : ANE (1 : 4)	Batch	-	30		10	<1	2	0.18	4.95 (7.30) 1.47	
Polymer 8	St : ANE (1 : 4)	Batch	-	30		8	1	2	0.19	4.80 (6.90) 1.44	
Polymer 9	St : ANE (1 : 4)	Batch	-	30		8	1	3	0.18	5.00 (7.50) 1.50	
Polymer 10	St : ANE (1 : 1)	Batch	-	8		18	<1	8	0.05	9.00 (20.2) 1.24	
Polymer 11	St : ANE (1 : 1)	Semi batch <sup>a</sup>	Toluene	1470 <sup>d</sup>		Investigation of the influence of the use of a semi batch process on the incorporation of ANE in the copolymer	60	12	6	0.15	6.00 (10.0) 1.67
Polymer 12	St : ANE (1 : 1*)	Semi batch <sup>a</sup>	Toluene	4350 <sup>e</sup>		84	6	5	0.19	4.60 (6.10) 1.31	
Polymer 13	MMA : ANE (1 : 0) [M] = 50 wt %	Batch	Toluene	180		Effect of ANE on the kinetic of MMA polymerization and ANE incorporation in the copolymer produced	98	-	98	-	28.1 (53.1) 1.89
Polymer 14	MMA : ANE (1 : 1)	Batch	Toluene	1380	95		4	48	**	11.9 (17.5) 1.47	
Polymer 15	MMA : ANE (1 : 0) [M]=26 wt %	Batch	Toluene	1380	>99		-	>99	-	7.20 (25.5) 3.54	
Polymer 16	MMA : ANE (1 : 1)	Batch	Toluene	90	Determination of the transfer constant of MMA to ANE	11	<1	5	0.01	60.5 (103) 1.69	
Polymer 17	MMA : ANE (1 : 2)	Batch	Toluene	120		10	<1	3	0.02	41.6 (62.1) 1.49	
Polymer 18	MMA : ANE (1 : 0.25)	Batch	Toluene	60		10	<1	8	**	73.9 (135) 1.82	
Polymer 19	2EHA : ANE (1 : 0)	Batch	Toluene	120	Effect of ANE on the kinetic of 2EHA polymerization, in the copolymer produced and rough estimation of the reactivity ratios of 2EHA and ANE.	99	-	99	-	15.4 (73.8) 4.79	
Polymer 20	2EHA : ANE (5 : 1)	Batch	Toluene	1470		94	57	88	0.15	13.5 (28.4) 2.10	
Polymer 21	2EHA : ANE (1 : 1)	Batch	Toluene	1290		75	31	56	0.31	10.3 (15.6) 1.51	
Polymer 22	2EHA : ANE (1 : 9)	Batch	-	30	Accurate determination of reactivity ratios of the 2EHA & ANE and determination of the transfer constant of P2EHA to ANE	2	<1	<1	0.48	7.90 (11.0) 1.33	
Polymer 23	2EHA : ANE (1 : 9)	Batch	-	30		2	1	1	0.43	8.90 (11.8) 1.25	
Polymer 24	2EHA : ANE (1 : 9)	Batch	-	30		2	<1	<1	0.45	7.90 (9.90) 1.28	
Polymer 25	2EHA : ANE (1 : 9)	Batch	-	30		4	1	1	0.50	7.80 (10.0) 1.28	
Polymer 26	2EHA : ANE (35 : 65)	Batch	-	80		21	6	11	0.35	11.9 (19.2) 1.61	
Polymer 27	2EHA : ANE (35 : 65)	Batch	-	60		15	2	7	0.34	12.5 (20.4) 1.63	
Polymer 28	2EHA : ANE (35 : 65)	Batch	-	60		15	3	8	0.34	12.7 (20.5) 1.61	
Polymer 29	2EHA : ANE (35 : 65)	Batch	-	60		15	4	8	0.33	13.1 (21.0) 1.60	
Polymer 30	2EHA : ANE (1 : 1)	Batch	-	40		17	6	12	0.28	17.8 (31.0) 1.74	
Polymer 31	2EHA : ANE (1 : 1*)	Semi batch <sup>b</sup>	Toluene	1470 <sup>d</sup>		Influence of the use of a semi batch process on the incorporation of ANE in the ANE-2EHA copolymer and to vary different parameters (monomer concentration and radical flux) to increase the rate of polymerization	53	28	41	0.36	12.7 (21.8) 1.72
Polymer 32	2EHA : ANE (1 : 1*)	Semi batch <sup>b</sup>	-	1470 <sup>d</sup>	66		41	53	0.37	11.0 (21.0) 1.91	
Polymer 33	2EHA : ANE (1 : 1*)	Semi batch <sup>c</sup>	-	1470 <sup>d</sup>	50		34	42	0.36	10.4 (24.9) 2.39	
Polymer 34	AA : ANE (1 : 0)	Batch	1,4 dioxane	30	Effect of ANE on the kinetic of AA polymerization, ANE incorporation in AA/ANE copolymerization and rough estimation of the reactivity ratios of AA & ANE	93	-	93	-	27.1 (141) 1.22 <sup>g</sup>	
Polymer 35	AA : ANE (4 : 1)	Batch	1,4 dioxane	1230		98	82	95	0.21	11.0 (39.9) 3.08 <sup>g</sup>	
Polymer 36	AA : ANE (1 : 1)	Batch	1,4 dioxane	1330		83	31	57	0.31	7.70 (20.3) 2.64 <sup>g</sup>	
Polymer 37	AA : ANE (45 : 55)	Batch	1,4 dioxane	30	Accurate determination of reactivity ratios of the ZAA & ANE and determination of the transfer constant of PAA to ANE	3	<1	1	0.26	9.60 (19.1) 1.99 <sup>g</sup>	
Polymer 38	AA : ANE (45 : 55)	Batch	1,4 dioxane	30		8	<1	3	0.28	14.2 (23.4) 1.65 <sup>g</sup>	
Polymer 39	AA : ANE (45 : 55)	Batch	1,4 dioxane	30		7	2	4	0.28	9.69 (20.1) 2.09 <sup>g</sup>	
Polymer 40	AA : ANE (1 : 4)	Batch	1,4 dioxane	90		10	<1	1	0.38	3.55 (6.90) 1.62 <sup>g</sup>	
Polymer 41	AA : ANE (1 : 4)	Batch	1,4 dioxane	90		5	1	2	0.35	3.35 (6.60) 1.94 <sup>g</sup>	
Polymer 42	AA : ANE (1 : 4)	Batch	1,4 dioxane	90		11	1	3	0.37	3.35 (6.91) 1.97 <sup>g</sup>	
Polymer 43	AA : ANE (1 : 9)	Batch	1,4 dioxane	60		7	1	1	***	1.85 (3.00) 1.62 <sup>g</sup>	
Polymer 44	AA : ANE (45 : 55)	Batch	1,4 dioxane	30		Determination of the transfer constant of AA to ANE at 70 °C	7	2	4	0.24	9.90 (19.7) 1.99 <sup>g</sup>
Polymer 45	AA : ANE (1 : 4)	Batch	1,4 dioxane	30		6	3	4	0.29	2.80 (5.50) 1.96 <sup>g</sup>	
Polymer 46	AA : ANE (1 : 9)	Batch	1,4 dioxane	90		<1	<1	<1	0.30	1.55 (2.20) 1.4 <sup>g</sup>	

**Reaction conditions:** Initiator used, ACHN for Polymer 1-43 and AIBN for Polymer 44-46; [Initiator] = 1 mol% relative to monomer used; Temp of reaction- Polymer 1-32 at 95 °C, Polymer 33-43 at 90 °C and Polymer 44-46 at 70 °C.

<sup>a</sup>ANE + 4 % of St in batch, ACHN + 96 % of St fed together; <sup>b</sup>ANE and part of the toluene in batch, 2EHA and (ACHN + toluene) fed separately; <sup>c</sup>ANE, toluene and ACHN in batch, 2EHA fed; <sup>d</sup>1440 min of feeding and <sup>e</sup>4320 min of feeding; <sup>f</sup>[M] = 50wt% when solvent was used; <sup>g</sup>methylated polymers.

\* Semi batch experiments. The ratio vinyl : ANE was calculated taking into account the full amount of monomers (both in batch and fed)

\*\*Signal not visible on <sup>1</sup>H NMR spectra

\*\*\*<sup>1</sup>H NMR spectrum too noisy to determine the copolymer composition

#Polymers were reprecipitated 3 times before GPC analysis and consequently, oligomers were lost. Therefore,  $M_n$ ,  $M_w$ , and dispersities values are biased.

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## Gel Permeation Chromatography

Size exclusion chromatography (SEC) was conducted on a Viscotek TDAmx consisting of a GPCmax integrated solvent and sample delivery module, a TDA 302 Triple Detector Array, and OmniSEC software. 2 x PLgel 5  $\mu\text{m}$  Mixed-C (200-2,000,000) columns were applied in sequence for separation. The instrument was calibrated with polystyrene standards (PL2010-0100 Polystyrene calibration kit, S-M-10) purchased from Agilent. This sets included standards of 580, 1300, and 5000 Da, among others. THF was used as the eluent at 1.0 mL/min with column and detector temperature at 30  $^{\circ}\text{C}$ , molecular weight values were determined against poly(styrene) standards.

Prior to analyses, PAA and P(AA-co-ANE) were methylated as follows: 25 mg of polymer were weighted and dissolved into 1 mL of milliQ water and 2 mL of THF. Then, (trimethylsilyl) diazomethane was added dropwise until full methylation (this was visible as an excess of (trimethylsilyl) diazomethane gave a yellow colour to the sample). Then, the methylated polymers were dried with a rotary evaporator and in a vacuum oven.

## Results and Discussions

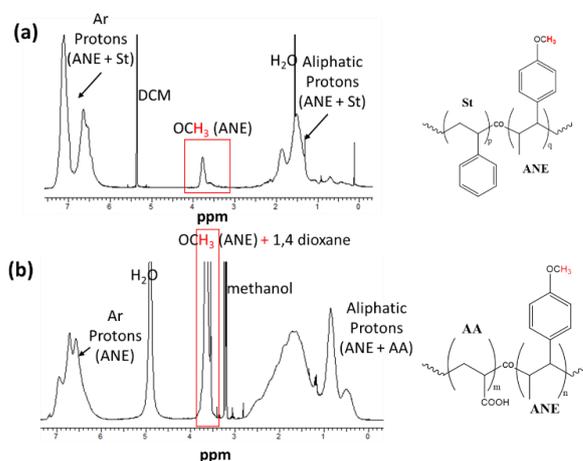
All polymers were analysed by GPC analyses. The [number-average molecular weight](#)  $M_n$ , weight-average molecular weight  $M_w$  as well as the dispersity were determined. Final conversions and copolymer compositions were determined by  $^1\text{H}$  NMR Spectroscopy. Results are presented in table 1. Examples of  $^1\text{H}$  NMR spectra are given in figure 1. More details on signal assignments are given in ESI.

From table 1, we observe that the presence of ANE has different effects on the polymerization of vinyl monomers. These effects will be detailed below.

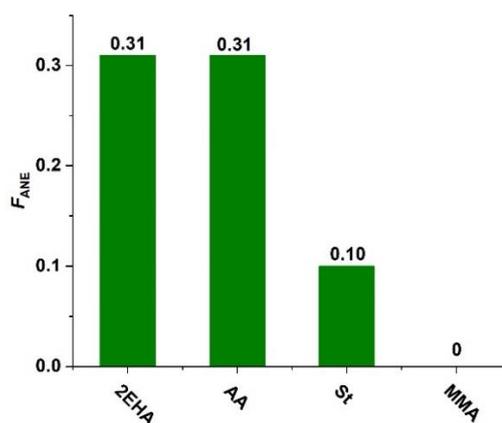
## Effect of ANE on the polymerization of St, MMA, 2EHA, AA.

St, MMA, 2EHA and AA were homopolymerized and copolymerized with ANE (Scheme 1). When the copolymerization was carried out in toluene and with a molar ratio vinyl monomer : ANE = 1 : 1, fraction of ANE in copolymer produced ( $F_{\text{ANE}}$ ) values were different in P(St-co-ANE), P(MMA-co-ANE), P(2EHA-co-ANE), and P(AA-co-ANE). (see figure 2). For MMA : ANE copolymerizations,  $^1\text{H}$  NMR analyses did not allow confirming the presence of ANE units. This is likely due to the steric hindrance, both methylene group of MMA and ANE are substituted. AA and 2EHA have very similar reactivity toward ANE, even though the polymerizations were carried out in different solvents (1,4-dioxane for AA and ANE and toluene for 2EHA and ANE). This confirms the previous results obtained by Nonoyama *et al.*

who copolymerized MA, nBA and tBA with ANE. Even though a slight effect was observed in fluorinated solvents, they did not observe an effect of the bulkiness of the acrylate ester side group on ANE incorporation when experiments were carried out in toluene. Moreover, they also observed 31 % of acrylate incorporation<sup>21</sup>. The lower reactivity of styrene toward ANE may be due to an electronic effect. ANE is an electron-donor. 2EHA and AA are electron acceptor while St is also a donor. Finally, it needs to be stressed out that even though the conversions of St, MMA, 2EHA, and AA are above 80 %, there are significant differences (>10 %) between these final conversions. Consequently, these experiments just provide a crude indication of comonomer incorporation.



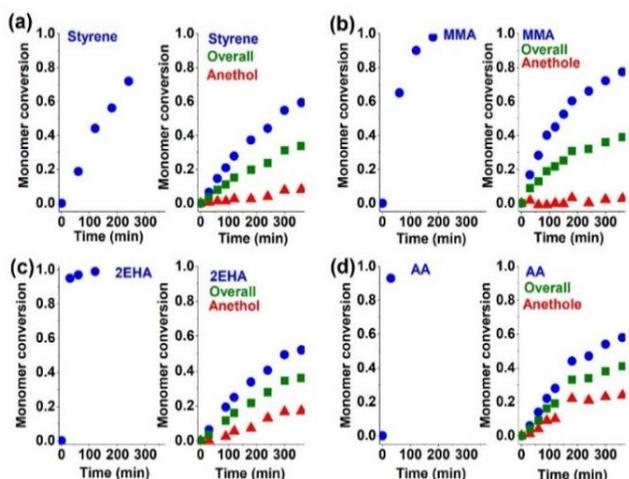
**Figure 1:** Partial  $^1\text{H}$  NMR spectra of (a) P(St-co-ANE) (polymer 3) purified, analysed in dichloromethane- $d_2$ , (b) P(AA-co-ANE) (polymer 36), analysed in methanol- $d_4$ .



**Figure 2:** Fraction of ANE incorporated in vinyl based copolymers (polymers 21, 36, 3 and 14 respectively)

From the results presented in Table 1, it is observed that introducing ANE in the batch copolymerization retard the polymerization of vinyl monomers. From table 1 we also observe that it takes longer time to reach high conversion for the copolymerization with higher fraction of ANE in monomer feed ( $f_{ANE}$ ).

Figure 3 compares the rate of polymerization of the four vinyl monomers when they are homopolymerized and copolymerized with ANE. Raw data are in ESI (tables S2 to S12). A very fast homopolymerization of AA and 2EHA is observed. An unintentional temperature increase cannot be excluded.



**Figure 3:** Kinetic of homo and copolymerization of (a) St (polymer 1) and St : ANE (polymer 3), (b) MMA (polymer 13) and MMA : ANE (polymer 14), (c) 2EHA (polymer 19) and 2EHA : ANE (polymer 21), (d) AA (polymer 34) and AA : ANE (polymer 36). Errors in partial monomer conversions 2%.

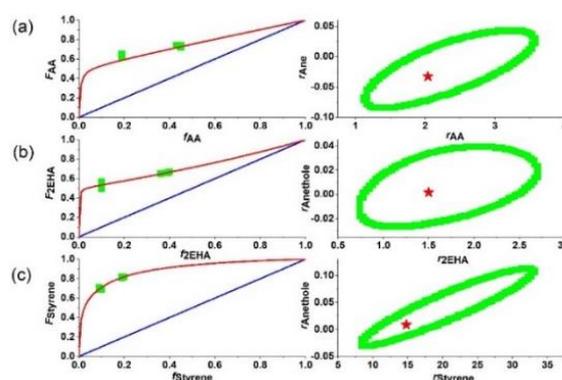
We note that the more ANE is incorporated in the polymer chain, the stronger is the retarding effect. This could be due to the (i) slower reactivity of ANE radical compared to that of the St, 2EHA, AA, MMA radicals toward St, 2EHA, MMA, and AA monomers respectively and (ii) the transfer effect of ANE due to its allylic hydrogen, which will be detailed later.

Reactivity ratios with a 95 % joint confidence interval were evaluated (except MMA-ANE pair as the ANE incorporation is too low in copolymer produced for accurate NMR measurement) using the nonlinear least squares (NLLS) method with the CONTOUR software package<sup>36</sup>. From the conversion monitoring, a first estimation of the reactivity ratios was obtained from the copolymerizations of AA, 2EHA and St with ANE at a molar ratio of 1 : 1 with the NLLS method applied to compositional drift data. The method is described elsewhere<sup>22</sup>. With these first estimates, according to the Tidwell-Mortimer criterium, two fractions of ANE in monomer feed ( $f_{ANE}$ ) values were calculated, allowing the most accurate determination of reactivity ratios by the software<sup>37</sup>. Experiments were conducted accordingly in bulk and at 95 °C for the systems 2EHA : ANE and St : ANE, and in 1,4-dioxane and at 90 °C for the system AA : ANE. Reactions were quenched at low monomer conversion (<0.1) to

avoid composition drift. More information is provided in ESI (tables S13 to S16). Results are presented in table 2 and in figure 4. In every case,  $r_{ANE}$  is equal to zero within experimental error, which confirms that ANE does not homopolymerize. AA, 2EHA and St radicals have a preference to react with AA, 2EHA and St monomers respectively in comparison to ANE.

**Table 2:** Reactivity ratios of systems AA : ANE, 2EHA : ANE, St : ANE. Errors are standard deviations as inferred from the true (asymmetric) joint confidence intervals (see Figure 4).

System	Reactivity ratios
AA : ANE	$r_{AA}=2.070$ (-0.441, +0.705) $r_{ANE}=-0.033$ (-0.027, +0.38)
2EHA : ANE	$r_{2EHA}=1.500$ (-0.388, +0.612) $r_{ANE}=0.002$ (-0.014, +0.019)
St : ANE	$r_{St}=14.796$ (-3.248, +9.385) $r_{ANE}=0.009$ (-0.020, +0.053)



**Figure 4:** Mayo plots (left) and reactivity ratios with the 95 % joint confidence interval (right) of systems (a) AA : ANE, (b) 2EHA : ANE, and (c) St : ANE.

#### Effect of a semi batch process on the copolymerization of ANE with vinyl monomers

It is known that a batch process in free radical copolymerization will normally result in composition drift and, therefore, a copolymer composition distribution. One monomer called “fast” monomer is consumed quicker than the other. At early stages of the polymerization, polymer chains rich in fast monomer will be formed while toward high conversion, the slower monomer will be more incorporated. ANE is a “slow” monomer in comparison to AA, 2EHA and St. In order to enhance the incorporation of ANE, we tested semi batch processes for the systems 2EHA : ANE and St : ANE. Addition feeding profile were determined with the MAP software package<sup>21</sup>. The MAP routine is utilizing reactivity ratios to predict the semi-batch monomer feed profiles on conversion basis. We then assume a conversion-time rate relation and take samples to measure the actual conversion-time relation which leads to a next iteration. Usually within 2-3 iterations we derive the optimal addition profile on time basis. The calculation indicated that about 4 % of the 2EHA and St should be in the batch at t=0. The profiles are in ESI (figures S3 and S4). However, as ANE does not homopolymerize, we decided

to feed all the 2EHA in the case of 2EHA : ANE copolymerization, which should not make any difference. Results are presented in table 3.

Using a semi batch experiment has allowed improving ANE incorporation both in P(St-co-ANE) and P(2EHA-co-ANE) (Table 3). However, we observe that the use of a semi batch experiment is more efficient with the St : ANE system than with the 2EHA : ANE system as (i) an increase of  $F_{ANE}$  from 0.10 to 0.15 (33 %) was observed vs from 0.31 to 0.36 (16 %) in the system 2EHA : ANE and (ii) both molecular weight and dispersity are reduced in the case of St : ANE in contrast to the system 2EHA : ANE. These decreases are consistent with previous results<sup>27</sup>. In our previous study<sup>27</sup>, semi batch experiments lead to lower  $M_w$  and dispersities as the monomer concentration throughout the reaction is lower than initially in batch. Here, results are different. Two explanation are possible: (i) the initiator feeding strategy is different, (ii) the loss of oligomers occurring during purification steps. The discrepancy between the systems St : ANE and 2EHA : ANE is likely due to the reactivity ratios values. When copolymerized with ANE,  $r_{St} = 14.796$  (-3.248, +9.385) and  $r_{2EHA} = 1.500$  (-0.388, +0.612). The preference of 2EHA radicals for 2EHA monomers vs ANE monomers is much less pronounced than the preference of St radical for St monomers vs ANE monomers. Without a semi batch process, 2EHA and ANE copolymerize already well together (31 % of ANE incorporation). Figure 5 shows that batch polymerization of St and ANE leads to a significant composition drift. This composition drift is largely reduced initially due to the use of a semi batch experiment. Feeding profiles usually have a trade-off in the form of longer reactions times due to the lower monomer concentration present on average during the polymerization. For the system 2EHA : ANE, the drift is present but less pronounced. Consequently, a semi batch approach is not as useful. In both cases, the use of a semi batch process allows maintaining the produced copolymer composition constant for a certain time, but after several hours of reaction, the composition drift is observed again. This is due to the decrease of the rate of vinyl polymerization due to the presence of ANE. As explained previously, ANE is a retarder of vinyl monomers polymerization. To avoid that situation, the feeding time should be increased up to a point where a semi batch process would not be advantageous anymore. This effect should be more pronounced in the 2EHA : ANE system as more ANE is incorporated and so the kinetic of 2EHA consumption is more affected.

We observe that the 2EHA and St final conversions are lower in a semi batch process than in a batch polymerization, using similar reaction times. This is not a surprise as monomer concentration is lower in semi batch experiments. Different polymerization parameters were modified to improve the semi batch experiments; monomer concentration, radical flux – by placing the initiator in the batch rather than in the syringe- and feeding rate. Only a slower feeding allowed a non-negligible increase of ANE incorporation. By feeding for 72 hours instead of 24 hours,  $F_{ANE}$  was increased from 0.15 up to 0.19.

Interestingly, it is possible to compare the results obtained for the 2EHA : ANE copolymerization in this study with our previous results

obtained for 2EHA : 2-methylene-1,3 dioxepane (MDO) copolymerization from our previous study<sup>27</sup>. For both systems, reactivity ratios ( $r_{2EHA}=1.507$  (-0.434, +0.854) and  $r_{MDO}=0.002$  (-0.116, +0.171)) and addition feeding profile were almost identical. However, the use of a semi batch process for the system 2EHA : MDO was a great success (significant increase of MDO units, lower dispersity, almost full consumption of both monomers, and almost no composition drift during the full process even though MDO was fed quicker: 5 hours rather than 25 hours).

The MAP software package may predict the optimal addition feeding profile (based on reactivity ratios and monomer physical properties) on conversion basis, but cannot predict whether or not such an experiment will significantly improve the “slow” monomer incorporation and the monomer consumption within a reasonable feeding time. Reactivity ratios, expressed as follows determine the optimal addition feeding profile for a semi batch experiment.

$$r_{fast} = \frac{k_{fast-fast}}{k_{fast-slow}} \quad (4)$$

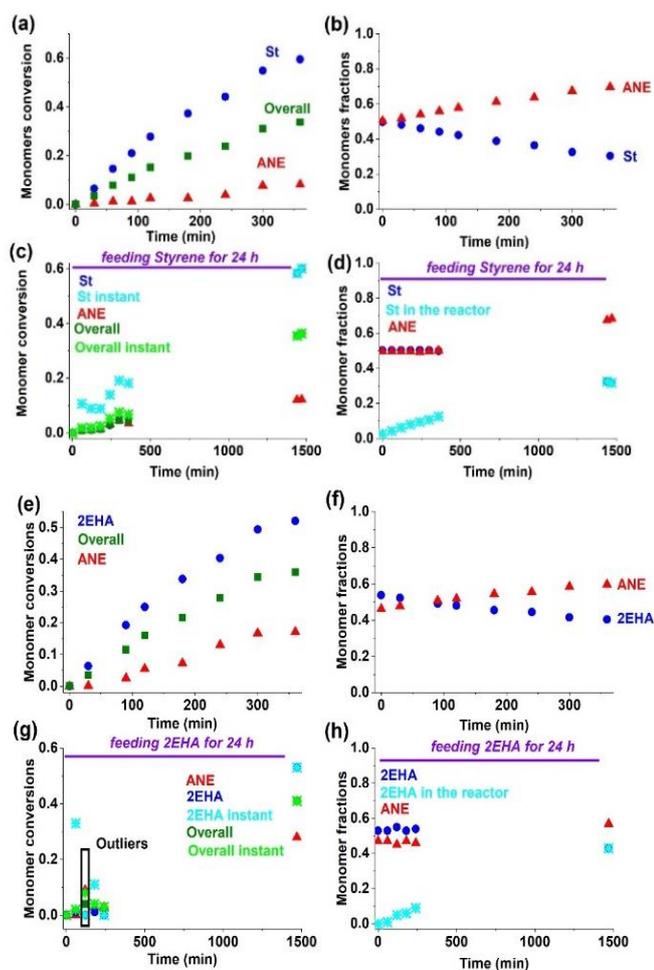
$$r_{slow} = \frac{k_{slow-slow}}{k_{slow-fast}} \quad (5)$$

In these expression, the slow monomer has the lower reactivity ratio.  $k_{slow-slow}$  and  $k_{fast-fast}$  are the homopropagation rate coefficients and  $k_{slow-fast}$  and  $k_{fast-slow}$  are the cross propagation rate coefficients. The  $k_{slow-fast}$  is the parameter which likely determines whether or not a semi batch experiment will significantly improve both monomer consumption and incorporation of slow monomer units in the copolymer chains within a reasonable time! In both systems,  $r_{slow}$  is close to zero. This value does not allow an estimation of the  $k_{slow-fast}$ . In the case of 2EHA : MDO copolymerization, the presence of MDO radicals boosted the rate of 2EHA consumption. As a result, most 2EHA was consumed as soon as introduced in the batch via the feeding pump. Consequently, (i) maintenance of monomer composition, (ii) formation of copolymer chains with similar composition, (iii) higher monomer consumption was observed. For the 2EHA : ANE system, ANE radicals slow down the 2EHA consumption and the consequences were described above.

In the future, for such copolymerization systems ( $r_{fast} > 1$  and  $r_{slow} \approx 0$ ), it will be important to test the effect of addition of the slow monomer on the rate of consumption of the fast monomer to determine whether or not semi batch experiments can significantly improve a copolymerization process.

**Table 3:** Comparison of copolymers obtained with a batch and with a semi batch process.

Code	System	Process	[M] in Toluene	Initiator location	React. Time (min)	Feed time (min)	St or 2EHA conv. (%)	ANE conv. (%)	Overall conv. (%)	$F_{ANE}$	$M_n$ , kDa; ( $M_w$ , kDa); Dispersity
Polymer 3	St : ANE (1:1) St: 5.01 g ; ANE: 7.12 g and Toluene: 14 mL	Batch	50 wt %	In batch	1350	-	81	09	44	0.10	6.5 (15.7) 2.42
Polymer 11	St : ANE (1:1) Batch- (St:220 $\mu$ l; ANE: 7.11 g and Toluene: 14 mL); 4.8 g of St and 234.6 mg of ACHN were fed	Semi batch	50 wt %	fed	1470	1440	60	12	36	0.15	6.0 (10.0) 1.67
Polymer 12	St : ANE (1:1) Batch- (St: 604.3 mg ; ANE: 21.3 g and Toluene: 42 mL); 14.4 g of St and 704 mg of ACHN were fed	Semi batch	50 wt %	fed	3450	3420	84	6	45	0.19	4.6 (6.1) 1.31
Polymer 21	2EHA : ANE (1:1) 2EHA: 3.04 g ; ANE: 2.42 g and Toluene: 6.2 mL	Batch	50 wt %	In batch	1290	-	75	31	56	0.31	10.3 (15.6) 1.51
Polymer 31	2EHA : ANE(1:1) Batch- (4.02 g of ANE and Toluene: 4.64 mL); 5 g of 2EHA and (141.7 mg of ACHN and 5.17 mL of Toluene) were fed simultaneously	Semi batch (co-feeding)	50 wt %	fed	1470	1440	53	28	41	0.36	12.7 (21.8) 1.72
Polymer 32	2EHA : ANE(1:1) Batch- (ANE: 4.02 g); 4.98 g of 2EHA and (132.6 mg of ACHN and 1 mL of Toluene) were fed simultaneously	Semi batch (co-feeding)	Bulk	fed	1470	1440	66	41	53	0.37	11.0 (21.0) 1.91
Polymer 33	2EHA : ANE (1:1) Batch- (ANE: 4.02 g and ACHN: 136.4 mg); 4.98 g of 2EHA was fed	Semi batch	Bulk	In batch	1470	1440	50	34	42	0.36	10.4 (24.9) 2.39

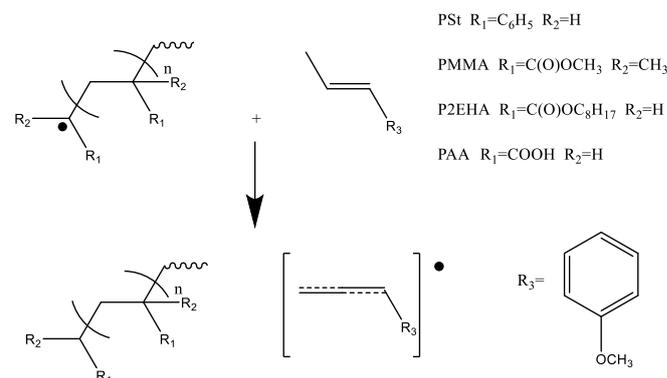


**Figure 5:** Evolution of monomer conversions and of monomer fractions vs time for (a) and (b) St : ANE copolymerization in batch (polymer 3), (c) and (d) St : ANE copolymerization in semi batch (polymer 11), (e) and (f) 2EHA : ANE copolymerization in batch (polymer 21), (g) and (h) 2EHA : ANE copolymerization in semi batch. Raw data are in ESI (tables S4 and S10). For polymers 3 and 11, the evolution of monomer conversion and of monomer fractions are presented only during the first 6 h and not until the polymerization was quenched.

## Side reactions

**Effect of ANE incorporation on the molecular weight of poly(vinyl-co-ANE)** From the values in table 1, we note that the higher the amount of ANE in the batch, the higher the fraction of ANE in the copolymer, and the lower the  $M_n$  and  $M_w$ . It could be due to a faster termination by combination of ANE and other vinyl radicals. A more plausible explanation is the potential of ANE to play a role as chain transfer agent (CTA). Transfer to monomer is particularly important with monomers containing allylic hydrogens, such as propylene, because the formation of resonance-stabilized allylic radicals is highly favourable (see scheme 2). For instance, high-molecular-weight polypropylene cannot be prepared using conventional free

radical polymerization. Consequently, the structure of ANE strongly favours transfer to monomer.

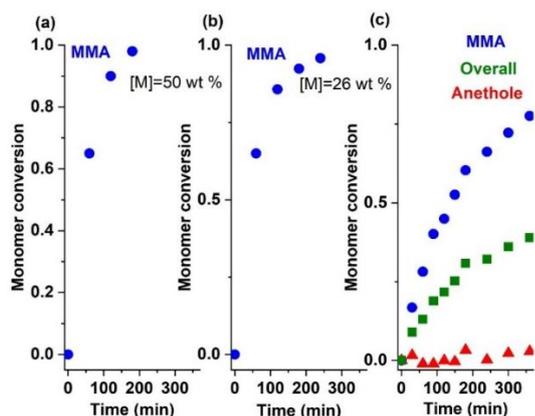


**Scheme 2:** Transfer to monomer containing allylic hydrogen.

More interestingly, even though no ANE incorporation in PMMA chain was observed, the kinetic of MMA polymerization was significantly affected by the presence of ANE in the batch. To be sure that ANE did not act as a solvent, a MMA homopolymerization in which ANE was replaced mole to mole by toluene (polymer 15, Table 1) was carried out. In this case, with no ANE present, a quicker MMA consumption is observed (see Figure 6). This small decrease of rate of monomer consumption in the presence of a CTA is not unusual. Shorter chains are formed and there is an increase of termination rate coefficient  $k_t$  (chain length dependent termination). The rate of polymerization is proportional to  $k_p/k_t^{0.5}$ . This was observed for AA polymerized with 2-mercaptoethanol<sup>38</sup>. These observations lead to the conclusion that ANE is not only a comonomer, but possibly also a CTA with a slower re-initiation coefficient.

**Table 4:** Transfer from St, MMA, 2EHA, AA to ANE: values of  $C_T$  with the correlation coefficient obtained on the plot  $1/DP_n$  vs  $[CTA]/[M]$

Polymers	PSt (95 °C)	PMMA (90 °C)	P2EHA (95 °C)	PAA (90 °C)	PAA (70 °C)
$C_T$ of transfer to ANE	0.0027	0.00062	0.0012	0.0066	0.0063
Standard deviation	$4 \times 10^{-4}$	$1 \times 10^{-4}$	$3 \times 10^{-4}$	$4 \times 10^{-4}$	$7 \times 10^{-4}$
Correlation coefficient $R^2$	0.97	0.98	0.93	1.00	0.99

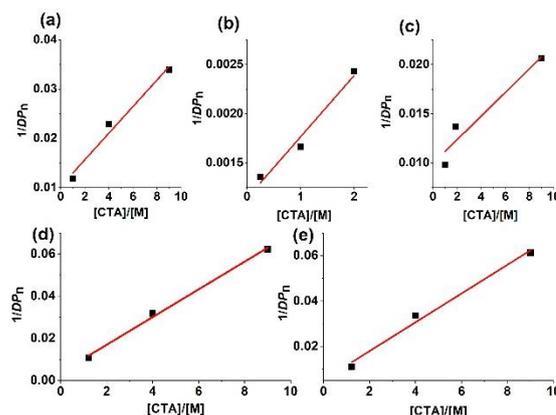


**Figure 6:** Monomer conversion vs time for the syntheses of (a) polymer 13 (MMA homopolymerization in toluene with  $[MMA]=50$  wt %), (b) polymer 15 (MMA homopolymerization in toluene with  $[MMA]=26$  wt %), (c) polymer 14 (attempt to copolymerize MMA and ANE in toluene with  $[monomers]=50$  wt % and  $[MMA]=20$  wt %). Raw data are in ESI (tables S5 to S7).

The transfer constants  $C_T$  – defined as the ratio of the transfer rate coefficient  $k_{tr}$  over the propagation rate coefficient  $k_p$  – were determined with the method of Mayo<sup>39</sup>. Results are presented in table 4 and Figure 7. Calculations were carried out taking into account the incorporation of ANE as comonomer. Details are in ESI (Equations S7 to S9 and table S17). For transfer from PMMA to ANE, experiments were designed especially for the  $C_T$  determination. In all other cases, the reactivity experiments performed for reactivity ratios determination were used, plus one more reaction to obtain a third data point. Three copolymerizations of AA and ANE were repeated at 70 °C to study the activation energy of the transfer constant to ANE. Consequently, the limit of these experiments are (i) the CTA is also a comonomer, (ii) the ratio  $[Initiator]/[Monomer]$  remain constant only if we consider the CTA as a monomer. The method of Mayo does not take into account such approximations. However, all correlation coefficients  $R^2$  obtained are close to unity, which indicate precise results.

The  $C_T$  values obtained are quite low (always  $<0.01$ ), however, when used as a comonomer at high concentration, it still has a considerable effect on molecular weight, dispersity and rate.

Figures 7 (d) and (e) show that changing the temperature does not affect the transfer from AA to ANE. This is consistent with the findings of Hutchinson et al. that the transfer constant to dodecanethiol has a low activation energy<sup>40</sup>. However, this conclusion need to be considered with high caution as (i) the small temperature range (only 20 °C) and (ii) the uncertainty of the values.

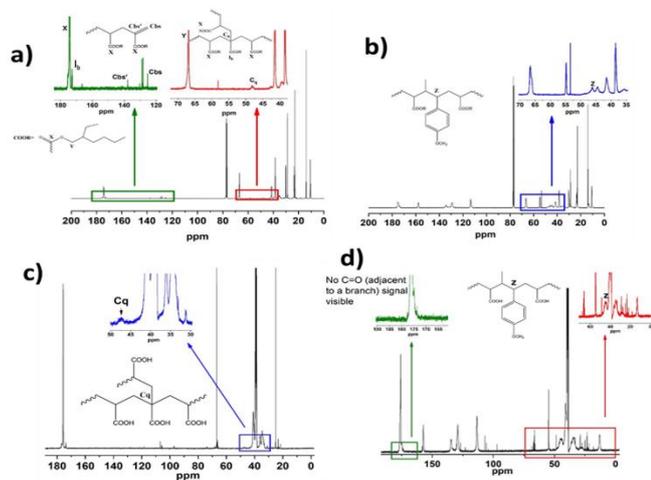


**Figure 7:** Plots  $1/DP_n$  vs  $[CTA]/[M]$  for (a)  $M = St$  and  $CTA = ANE$ , 95 °C (b)  $M = MMA$  and  $CTA = ANE$ , 90 °C (c)  $M = 2EHA$  and  $CTA = ANE$ , 95 °C (d)  $M = AA$  and  $CTA = ANE$ ,  $T = 90$  °C, (e)  $M = AA$  and  $CTA = ANE$ ,  $T = 70$  °C.

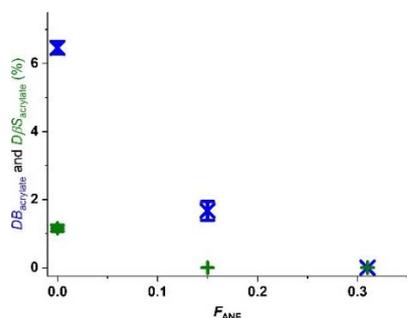
**Effect of Anethole incorporation on branching and beta fragmentation** Branching doesn't occur for PMMA nor PSt. It is well known that when produced by radical polymerization, PAA and poly(alkyl acrylates) are branched<sup>28-30, 41, 42</sup>. Long and short chain branches (LCB and SCB) were reported in the literature. Branching arises either from intramolecular transfer 1,5-H abstraction (also known as backbiting) and short branches can be formed by (i) intermolecular transfer to polymer (a H transfer between a dead chain and a living chain) and (ii) by random intermolecular transfer. In all these case, a midchain radical (MCR) is formed that propagate. During 2EHA polymerization, MCR can also undergo  $\beta$  fragmentation, leading to a SPR and a macro monomer. <sup>13</sup>C NMR spectroscopy analyses confirmed that homo PAA and homo P2EHA synthesized for this study at 90 °C and 95 °C respectively are branched and  $\beta$ -scission occur during 2EHA polymerization (figures 8 and 9).

Branching in P2EHA and PAA synthesized here were determined by the identification of quaternary carbon  $C_q$  present at a branching point (figure 8 a & c). Determination of branching in P(AA-co-ANE) and P(2EHA-co-ANE) were difficult due to the overlapping of quaternary carbon  $C_q$  with the C-Ar of a ANE unit. Therefore, branching were quantified using ester carbonyl adjacent to a branch  $I_b$  (figure 8). When copolymerized with ANE, we observe that the higher the amount of ANE in the batch, the lower the fraction of branching and  $\beta$ -scission in the 2EHA backbone. And if  $F_{ANE}$  reaches a certain value, both branching and  $\beta$ -scission are totally inhibited (figure 9). This was already observed in our previous study for poly(alkyl acrylate-co-MDO)<sup>27</sup>, but the reduction was less pronounced here. For intra molecular backbiting to occur, acrylate-acrylate-acrylate triads need to occur. Inserting ANE units in the chain reduce the probability of formation of such triads. These results prove that even at a monomer concentration of 50 wt %, backbiting (or intramolecular transfer to polymer) is the dominant process in branch formation<sup>43</sup>. The more important effect of ANE incorporation on branching can be due to the role of ANE as a CTA. It

is known that H transfer can occur between a CTA and a MCR, transforming a MCR into a dead chain. This is called the patching effect<sup>41</sup>. Moreover, if transfer to a CTA occurs, the lifetime of a SPR is shorter and the number of backbiting event is reduced<sup>44</sup>. The reduction of amount of branching due to the presence of a CTA is already known for both AA and 2EHA polymerization<sup>28, 29</sup>.



**Figure 8:** <sup>13</sup>C NMR spectra of a) P2EHA (polymer 19), b) P(2EHA-co-ANE) (polymer 21), c) PAA (polymer 34) and d) P(AA-co-ANE) (polymer 35).



**Figure 9:** Degree of branching and of  $\beta$ -scission in P2EHA and P(2EHA-co-ANE) (polymers 19, 20, 21).

## Conclusions

This study showed that even though ANE cannot homopolymerize, it can copolymerize with various vinyl monomers. The incorporation of bio-based ANE in the polymer chain depends on different properties of the vinyl comonomer such as electronic properties and steric hindrance. The incorporation of ANE can be improved using a semi batch process. ANE has different effects on the polymerization of vinyl monomers. First, it retards the kinetics of the comonomer as ANE radicals are less reactive, likely due to its steric hindrance. Second, it acts not only as a comonomer but also a CTA. Adding ANE in the batch will reduce the molecular weight and the dispersity of the final copolymer. Finally, in the case on AA and alkyl acrylates, it inhibits the number of backbiting event and so the formation of branches and the  $\beta$ -scission, which reduces the dispersity. The

incorporation of ANE can be improved using a semi batch process, however, with the usual trade-off of longer reaction times. In the future, it will be important to estimate the optimal feeding rate before considering a semi batch process. This work provides relevant information for systematic variation of reaction conditions which will help to optimize conditions for poly(vinyl-co-ANE) synthesis in various applications, including incorporation of a bio-based comonomer.

## Conflicts of interest

There are no conflicts to declare

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