

Synthesis and Photopolymerization of Acrylic Acrylate Copolymers

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ABSTRACT: Acrylate-functionalized copolymers were synthesized by the modification of poly(butyl acrylate-co-glycidyl methacrylate) (BA/GMA) and poly(butyl acrylate-co-methyl methacrylate-co-glycidyl methacrylate). ¹³C-NMR analyses showed that no glycidyl methacrylate block longer than three monomer units was formed in the BA/GMA copolymer if the glycidyl methacrylate concentration was kept below 20 mol %. We chemically modified the copolymers by reacting the epoxy group with acrylic acid to yield polymers with various glass-transition temperatures and functionalities. We studied the crosslinking reactions of

these copolymers by differential scanning calorimetry to point out the effect of chain functionality on double-bond reactivity. Films formed from acrylic acrylate copolymer precursors were finally cured under ultraviolet radiation. Network heterogeneities such as pendant chains and highly crosslinked microgel-like regions greatly influenced the network structure and, therefore, its viscoelastic properties. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 753–763, 2002

Key words: acrylic acrylate copolymer; free-radical polymerization; photopolymerization

INTRODUCTION

The copolymers poly(butyl acrylate-co-glycidyl methacrylate) (BA/GMA) and poly(butyl acrylate-co-methyl methacrylate-co-glycidyl methacrylate) (BA/MMA/GMA) used for modification are acrylic copolymers containing epoxy functional groups as pendant units that are very versatile and have been described in literature. Glycidyl methacrylate polymerizes with many (meth)acrylic monomers, and then, it introduces reactive epoxy functional groups into copolymer chains. By modifying epoxy groups, one can adjust the copolymer reactivities and properties on a wide range. Epoxy groups can be further reacted with amines for crosslinking,^{1–3} or they can be chemically modified to introduce new reactive functional groups along the copolymer chains. Pendant mercaptan groups are obtained by the reaction of the epoxy groups with thio-glycolic acid.⁴ Reactive (meth)acrylate double bonds are introduced by modification of the epoxy groups with (meth)acrylic acid.^{5,6} In this work, we reacted epoxy groups with acrylic acid (AA) to chemically modify acrylic copolymers with lateral reactive epoxy groups into acrylic acrylate copolymers containing reactive lateral double bonds.

Acrylic acrylate copolymers can be crosslinked by thermal or ultraviolet (UV) curing. The industrial importance of UV curing of acrylic monomers or oligomers is still increasing. Polymerization under UV radiation is used for coating wood, paper, plastic, and metal and for inks. The main advantages of UV curing are high productivity, low environmental pollution, and low energy consumption.⁷ Photopolymerization of multifunctional monomers provides an efficient method for the formation of highly crosslinked networks. The network structure that is created is very complex, especially because of its very heterogeneous nature.⁸ Bowman and coworkers have undergone numerous studies on the structural evolution of photopolymerized networks by studying the kinetics of reactions,⁹ by monitoring the radical concentrations within the networks during polymerization,¹⁰ and by using “living” radical polymerization.¹¹ They concluded that networks produced by the photopolymerization of multifunctional monomers contain very highly crosslinked regions, called *microgels*, as well as much less crosslinked regions that connect the microgels. This kind of network formation has been extensively studied by Dusek and coworkers.^{12,13} Structural heterogeneities broaden the relaxation spectra of polymer chains. Barbeau et al.¹⁴ demonstrated two levels of structure on photocured polyurethane acrylate (PUA) networks by using transmission electronic microscopy and small-angle X-ray scattering, explaining the broad viscoelastic relaxations. A low-temperature transition was related to the PU soft segments, whereas a high temperature transition was associated

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with the presence of acrylate microgel-like clusters connected with each other, forming a kind of spider web.

EXPERIMENTAL

Materials

Different copolymers with different molar masses and different compositions and propoxylated neopentyl glycol diacrylate (NPGPODA) were supplied by Cray Valley (Table I). All solvents (analytical grade) were received from SDS.

Chromium III diisopropyl salicylate (CrDIPS) was synthesized according to Le Blainvaux et al.¹⁵ A mixture of 4.65 g of chromium III triacetate (Carlo Erba), 13.5 g of 3,5-diisopropyl salicylic acid (Aldrich) and 300 mL of ethanol was heated to reflux for 3 h under nitrogen. Ethanol and by-products were evaporated under vacuum. A green powder was eventually obtained.

Instruments

We used size exclusion chromatography (SEC) to determine the average molar mass of the polymers. SEC was performed on a Waters device fitted with a double detection system (differential refractometer R401 and a UV detector operating at $\lambda = 254$ nm), with three columns with gel porosities of 10^4 , 10^3 , and 500 Å. We used Poly(butyl acrylate) standards (Polymer Source Inc.) instead of poly(styrene) standards to better represent the polymer structure. Tetrahydrofuran (THF) was chosen as the mobile phase with a flow rate of 1 mL/min. The glass-transition temperature T_g was measured with a Mettler differential scanning calorimetry (DSC) apparatus under argon flux, at a heating rate of $10^\circ\text{C}/\text{min}$ and samples of about 15 mg. T_g was determined as the onset of the T_g . The reactivity of acrylic acrylate copolymers was checked by thermal polymerization during DSC scan by adding 1 wt % of azobis(isobutyronitrile) (AIBN; Fluka). We compared measured exotherms to theoretical values, assuming that the standard heat of polymerization was 78 kJ/

mol for one acrylate double bond.¹⁶ ^1H - and ^{13}C -NMR spectra were measured at 25°C in CDCl_3 with a Bruker 250 MHz spectrometer. To determine the conversion of photopolymerized films, we conducted attenuated total reflectance infrared (ATR-IR) spectroscopy on a Magna-IR 550 Nicolet with an ATR attachment. Measurements were taken from 4000 to 600 cm^{-1} , with a 4 cm^{-1} resolution. Each measurement was an average of 32 scans. Peak at 985 cm^{-1} , corresponding to $\nu(\text{C}=\text{C})$, was chosen for double bonds, and peak at 945 cm^{-1} , relative to $\nu(\text{C}-\text{O}-\text{C})$, was taken as an internal reference. Conversion was calculated respect to the liquid polymer mixture according to the following equation:

$$\text{Conversion (\%)} = \left(1 - \frac{[\nu(\text{C}=\text{C})/\nu(\text{C}-\text{O}-\text{C})]_{\text{film}}}{[\nu(\text{C}=\text{C})/\nu(\text{C}-\text{O}-\text{C})]_{\text{liquid}}} \right) \times 100 \quad (1)$$

Dynamic complex viscosity (η^*) of acrylic polymers was determined from -50 to 120°C with a Rheometrics dynamic analyser RDA II, with parallel plates ($\phi = 25$ mm, gap ≈ 1.5 mm) with a frequency of 1 Hz. We used dynamic mechanical analysis (DMA) to study photopolymerized films using a Rheometrics solid analyser RSA II. Sample thickness was about 100 μm , width was 6 mm, and working length was 22.5 mm. Dynamic temperature scans were conducted at a frequency of 10 Hz from -80 to 150°C with 2°C steps.

Chemical modification of acrylic copolymers

We chemically modified the acrylic copolymers BA/GMA and BA/MMA/GMA by reacting the epoxy groups introduced along the acrylic chains by glycidyl methacrylate units with the acid groups of AA. Because the viscosity of the copolymers was low enough to allow accurate mechanical stirring, the reaction took place in bulk. The Acrylic copolymer was charged in a 250-mL reactor and heated up to 100°C under an argon blanket. Precise temperature regulation was given by an oil bath. We blended hydroquinone (0.3 wt %) with the copolymer to prevent any reaction of acrylic double bonds during heating. After the reactor temperature was stabilized for 30 min, AA and CrDIPS catalyst (0.4 wt %) were added. CrDIPS has been shown to be a very efficient and selective catalyst for epoxy/acid reactions.¹⁵ AA incorporation was ad-

TABLE I
Average Compositions and Molar Masses of the Copolymers Used

Momomer	Composition (%)	\bar{M}_n (g/mol)
BA/GMA	100/00	7500
BA/GMA	95/5	7500
BA/GMA	89/11	7500
BA/GMA	84/16	7500
BA/GMA	78/22	7500
BA/GMA	20/80	7500
BA/MMA/GMA	75/14/11	6200

For all copolymers, the polydispersity was about 2.5.

justed to obtain an $\frac{\text{Acid Value}}{\text{Epoxy Value}}$ of 1.05. We used the slight acid excess to prevent the potential reaction between the epoxy and the secondary hydroxyl group created during the chemical modification of the epoxy. Conversion was periodically checked by chemical titration of the copolymer samples. Titrations took place at room temperature. We measured the acid value by

titrating residual acid groups with sodium hydroxyl, using phenolphthalein as an indicator. The epoxy value was determined on a mixture of copolymer, dichloromethane, and 15 cm³ of a solution of tetraethyl ammonium bromide (20 wt % in acetic acid). We titrated the mixture with a perchloric acid solution (0.1N in acetic acid), using violet crystal as an indicator. We stopped the chemical modification of the epoxy groups by cooling the solution down to 4°C when the epoxy conversion was higher than 90%. Because of the CrDIPS, acrylic acrylate copolymers were slightly greenish at the end of the chemical modification.

Photopolymerization of acrylic acrylate copolymer precursors

We polymerized neat acrylic acrylate copolymer precursors or solutions of acrylic acrylate copolymers with a diacrylate reactive diluent (NPGPODA) by using UV radiation to obtain transparent films. CrDIPS present in acrylic acrylate copolymers did not lead to significant coloration of photopolymerized films. 2,2-dimethoxy-2-phenylacetophenone (DMPA; 1 wt %; Aldrich) was added to acrylic acrylate copolymers as a photoinitiator. Thin layers (about 100 μm thick) were cast with a bar coater on carefully cleaned glass plates. These films were passed 10 times through a high-power UV lamp Fusion System; mercury bulb, 120 W/cm) at a speed of 3 m/min. In these conditions, we checked by ATR-IR spectroscopy that all films had reached their maximum conversion. Samples were cut and removed from the glass substrate before being tested.

RESULTS AND DISCUSSION

Characterization of acrylic copolymers

Different copolymers with different compositions and about the same molar masses were received from Cray Valley (Table I). The composition and molar masses of the acrylic copolymers used for the study are supplied in Table I. The homogeneity of copolymers based on BA/MMA/GMA by mole were studied by ¹H-NMR. The composition was 75/14/11%. We precipitated it by incorporating more and more methanol to a solution of copolymer in THF. Several fractions with decreasing molar masses were collected. Samples were analyzed by ¹H-NMR. Spectra of the lowest and the highest molar mass fractions are compared in Figure 1, and peak assignment is shown in Table II.^{17,18} Sample compositions determined by ¹H-NMR are given in Table III. According to the ¹H-NMR results, composition remained the same whatever the molar mass of the copolymer fraction was. Slight differences between samples were always kept within experimental error.

Small traces of double bonds were noticed on the low molar mass fraction of the copolymer. Those traces were not present on the high molar mass fraction. Furthermore, because precipitation removed all potential residual monomers, double bonds traces could not be due to unreacted monomers. We assumed that double bonds were caused by termination mode. On the one hand only termination by disproportionation leads to the creation of a double bond of the type ~CH=CH~R. On the other hand, the average molar mass of chains terminated by disproportionation is about two times lower than those terminated by combination. Such chains should be especially present in the low molar mass fraction of the copolymer. This assumption was consistent with the fact that double bonds traces were present only in this fraction.

¹³C-NMR results showed a peak at δ = 123.7 ppm for both fractions, relative to the ~CN coming from the initiator used. On the low molar mass fraction, a clear peak at δ = 128.4 ppm was noticed, related to ~CH=CH~, and much smaller peaks were also distinguished at 126.4 and 138.2 ppm, attributed to >C=CH₂ and >C=CH₂, respectively. On the contrary, the peak at 128.4 ppm could hardly be seen on the high molar mass fraction, and no peak was present on the 126.4 or 138.2 ppm ranges. This confirmed that the presence of double bonds was significant only in the small molar mass fraction because of the termination mode. The >C=CH₂ peaks on this fraction indicated that head-to-head propagation occasionally occurred, even if the classical head-to-tail propagation mode was the most widely developed. SEC chromatograms did not show residual monomer peaks at the end of polymerization.

Due to the increase of molar mass, the physical properties of the acrylic copolymers changed. *T_g* increased when number-average molecular weight (*M_n*) increased. For the copolymers previously described (BA/MMA/GMA = 75/14/11 mol %), *T_g* was equal to -48°C when *M_n* = 4500 g/mol, but *T_g* reached -40°C when *M_n* = 30,000 g/mol. Figure 2 highlights the relationship of *T_g*⁻¹ for the acrylic copolymers on the basis of BA/MMA/GMA = 75/14/11 mol %. Experimental data were fitted by linear regression. The following simplified equation¹⁹ was verified:

$$\frac{T_g^\infty}{T_{g(M_n)}} = 1 + \frac{c}{M_n} \quad (2)$$

where *T_g*[∞] is the *T_g* of a polymer of molar mass equal to *M_n*, *T_g*[∞] is the *T_g* of a copolymer of the same composition with theoretical infinite molar mass, and *c* is a parameter taking into account segments mobility. For the studied system, *T_g*[∞] was found to be about -38.5°C.

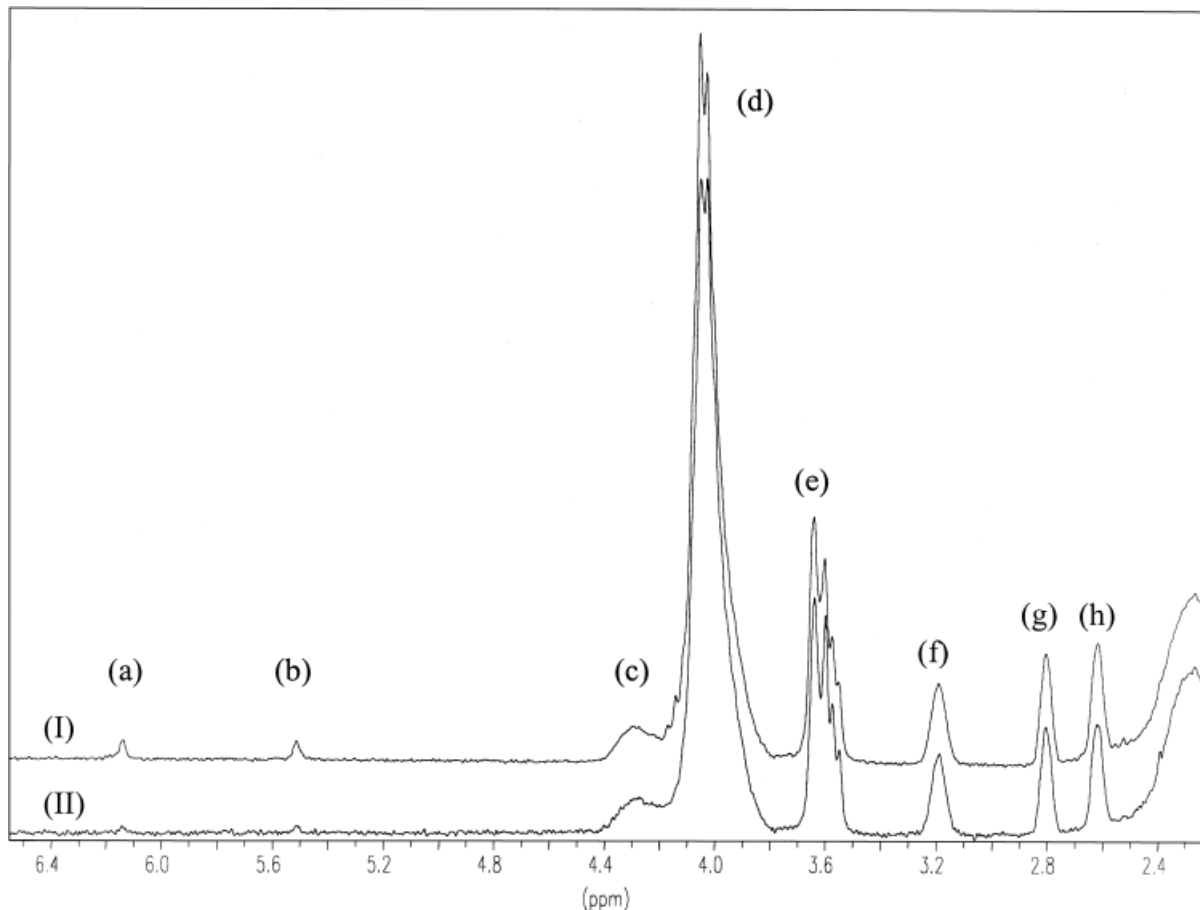


Figure 1 $^1\text{H-NMR}$ spectra of fractions of the copolymer of BA/MMA/GMA = 75/14/11 mol %: (I) low molar mass fraction and (II) high molar mass fraction.

Increasing molar mass also increased copolymer viscosity because of more chain entanglements. For a temperature of $T_g + 70^\circ\text{C}$, the relationship between the η^* and weight-average molecular weight (\bar{M}_w) showed a transition at the critical molar mass due to chain entanglements (\bar{M}_{crit}). A widely accepted empirical relationship shows that η^* is proportional to \bar{M}_w^a for linear copolymers and that the exponent a changes at \bar{M}_{crit} . For linear flexible copolymers, it has been shown in literature^{20,21} that \bar{M}_{crit} is directly proportional at the entanglement molar mass (\bar{M}_e). $\bar{M}_{\text{crit}}/\bar{M}_e$ is about 2.4. Theoretically, for $\bar{M}_w < \bar{M}_{\text{crit}}$, $\eta^* \propto \bar{M}_w$ and for $\bar{M}_w > \bar{M}_{\text{crit}}$, $\eta^* \propto \bar{M}_w^{3.4}$. Experimental data led to exponent values of 0.9 and 3.5 for low and high molar masses, respectively. \bar{M}_{crit} for the acrylic copolymer of composition BA/MMA/GMA = 75/14/11 mol % was equal to 32,500 g/mol. It was in same order of magnitude as \bar{M}_{crit} of poly(methyl methacrylate), which lays between 27,000²² and 30,000 g/mol.²³

By using polymers with different [BA]/[GMA] ratios from 100/0 to 80/20 mol %, we studied the effect of composition on various properties. The average molar mass of polymers was kept constant to $\bar{M}_n \approx 7500$ g/mol for all compositions because the same

synthesis conditions were used for all the syntheses. As shown in Figure 3, the increase of GMA concentration in the copolymer increased T_g . The relationship between the [BA]/[GMA] ratio of the copolymer and its T_g fit the following typical Fox's equation in the studied concentrations domain:

$$\frac{1}{T_g} = \frac{W_{\text{BA}}}{T_g^{\text{BA}}} + \frac{W_{\text{GMA}}}{T_g^{\text{GMA}}} \quad (3)$$

where W_{BA} and W_{GMA} are the weight fractions of BA and GMA, respectively, in the copolymer and T_g^{BA} and T_g^{GMA} are the T_g 's of BA and GMA homopolymers, respectively. T_g^{GMA} was found in literature to be equal to 76°C for $\bar{M}_n = 3100$ g/mol.²⁴ According to the correction due to the difference of molar masses, T_g^{GMA} was calculated to be close to 87°C for $\bar{M}_n = 7500$ g/mol.

The modification of the GMA concentration in the acrylic copolymer from 5 to 20 mol % changed the average epoxy functionality of copolymer chains from about 2.4 to 9.8. The average epoxy functionality of copolymer chains can be accurately used only if GMA does not form blocks but follows random distribution.

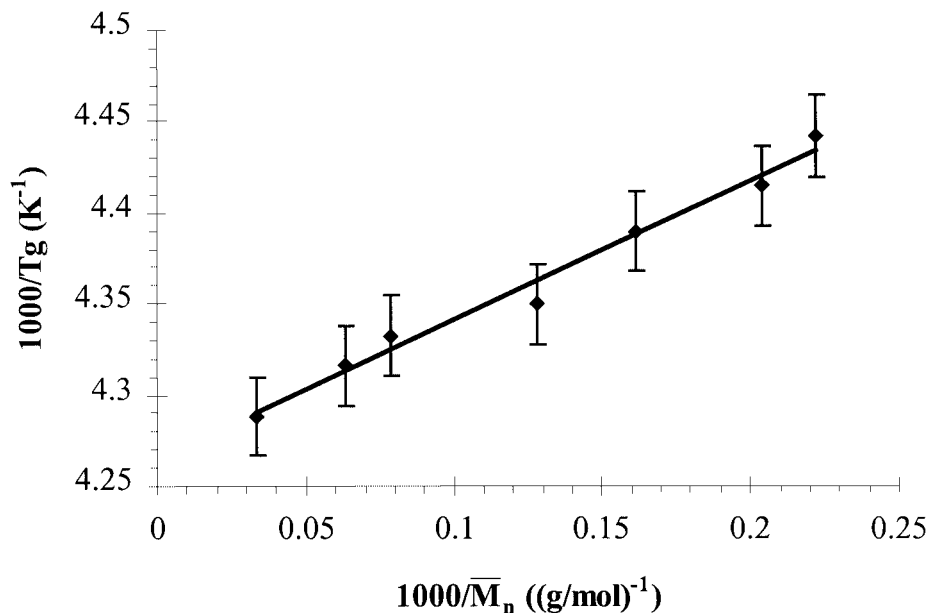


Figure 2 Effect of the molar mass on the onset of T_g of acrylic copolymers (BA/MMA/GMA = 75/14/11 mol %). The solid line corresponds to linear regression.

This calculated \bar{M}_v cannot be considered the real value due to the numerous pendant chains that were not elastically active. Results are summarized in Table IV. The decrease of maximal conversion came from the different chain mobility. For a multifunctional monomer, reactive groups became linked to the network from the beginning of the reaction, limiting the final conversion.²⁶ After crosslinking, DSC pans were put in THF for 2 weeks to extract potential unreacted linear copolymer chains. Solutions were filtered at 0.45

μm , and they were injected in SEC. A small peak corresponding to about 2% noncrosslinked polymer was found for the acrylic acrylate copolymer of $f = 2$. These nonreacted linear chains had low molar masses. Because maximal DSC conversion of acrylic groups of this sample was 100%, it can be concluded that a f of two double bonds per chain was not high enough to ensure at least one double bond on every copolymer chain. For f higher than 4, no more nonreacted linear copolymer chains were detected by SEC. In this case,

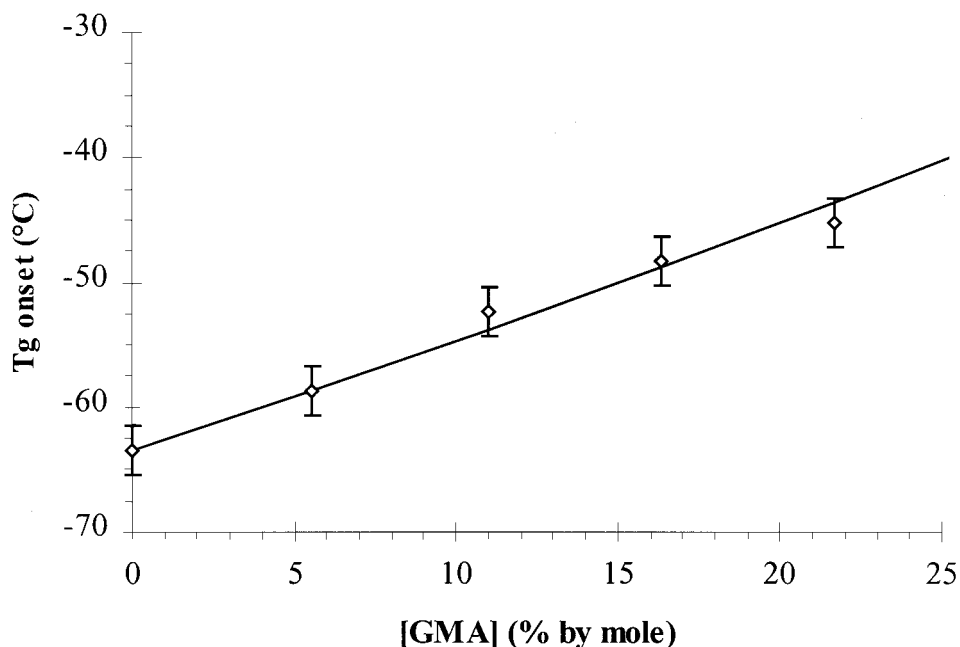


Figure 3 Variation of T_g of copolymers based on BA/GMA. [BA]/[GMA] ratio varied from 100/0 to 80/20 mol %; $\bar{M}_n \approx 7500$ g/mol. The solid line represents $1/T_g = W_{\text{BA}}/T_g^{\text{BA}} + W_{\text{GMA}}/T_g^{\text{GMA}}$.

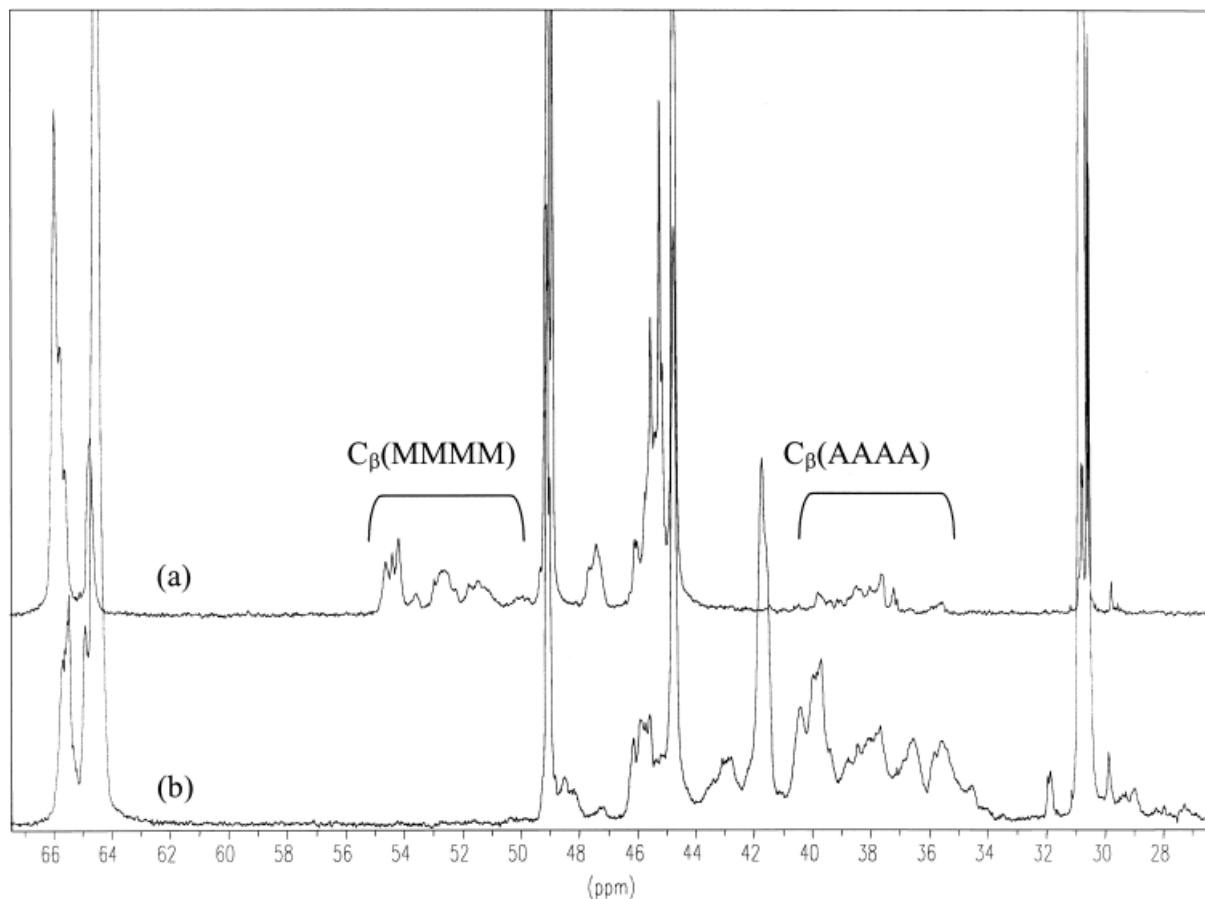


Figure 4 ^{13}C -NMR spectra of BA/GMA copolymers: (a) BA/GMA = 20/80 mol % and (b) BA/GMA = 80/20 mol %.

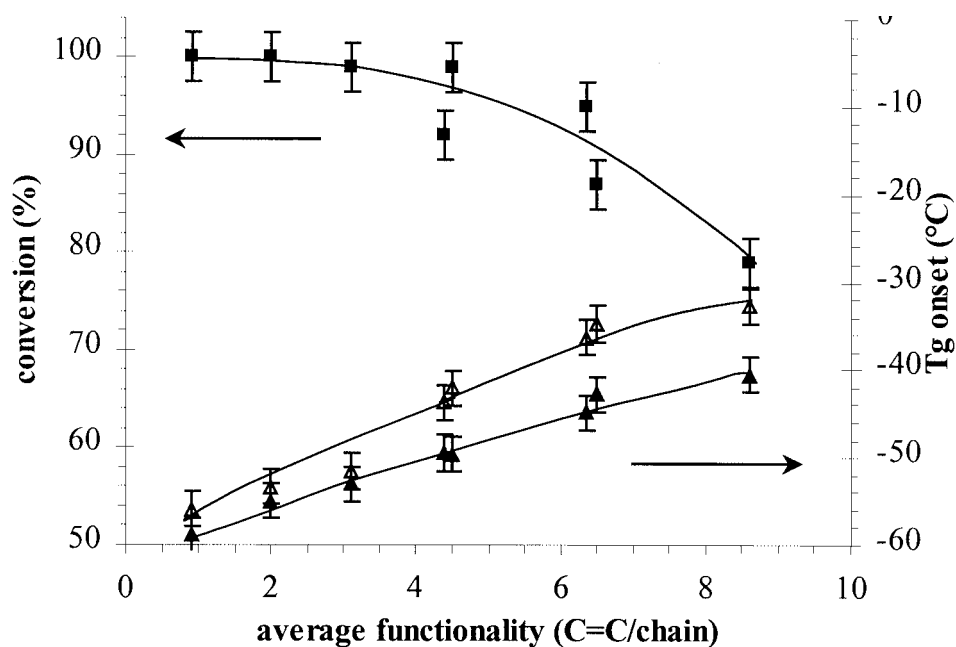


Figure 5 (■) conversion and T_g before crosslinking (▲) or after crosslinking (△) versus \bar{f} . Results from nonisothermal DSC scans (10°C/min) with 1 wt % AIBN. Acrylic acrylate copolymers were BA/GMA = 95/5 to 80/20 mol %; $\bar{M}_n \approx 7500$ g/mol.

TABLE IV
Effect of the \bar{f} of Acrylic Acrylate Copolymer Chains on Maximal Conversion and Networks Properties

\bar{f} (C=C/chain)	\bar{M}_n (g/mol)	Maximal conversion (%)	Increase of T_g (°C)	\bar{M}_v (g/mol)
0.9	7800	100	2.0	8650
2.0	7800	100	1.6	3900
3.1	7800	99	1.5	2550
4.4	7700	92	5.8	1900
4.5	7800	99	7.6	1750
6.4	8200	95	8.5	1350
6.5	7700	87	8.0	1350
8.6	8200	79	7.8	1200

all acrylic acrylate copolymer chains were linked to the network at least by one crosslink. In conclusion, for a given average molar mass, \bar{f} must be high enough to prevent the formation of nonreactive copolymer chains that cannot be linked to the network after polymerization.

Photopolymerized films based on acrylic acrylate copolymers

DMPA (1wt %) photoinitiator was blended with acrylic acrylate copolymers. Thin layers, about 100 μm thick, were cast on glass plates, and they were photocured. Dry transparent films were obtained. The effect of the average molar mass was evaluated with two copolymers of BA/MMA/GMA = 75/14/11 mol % with different molar masses (\bar{M}_n = 6200 or 30,000 g/mol). \bar{f} was equal to 5 for the low molar mass copolymer, and \bar{f} was 26 C=C/chain for the high molar mass copolymer. We tried to keep the average

molar mass per unsaturation constant around 1200 g/C=C. Final conversion of both films was about 80% as measured by ATR-IR, leading to $\bar{M}_c \approx 1500$ g/mol. Mechanical-transition temperature (T_α), defined as the maximum of the $\tan \delta$ peak raised from 28 to 40°C when \bar{M}_n increased from 6200 to 30,000 g/mol, as shown in Figure 6. The width of the $\tan \delta$ peak broadened for the high molar mass copolymer. It implied a wider distribution of relaxation times and a more heterogeneous network.²⁷ The modulus of the rubbery plateau at $T_\alpha + 50^\circ\text{C}$, noted E'_c , also slightly increased with the molar mass, changing from 15 to 21 MPa. Because \bar{M}_c was roughly the same for both networks, we assumed that the modification of the viscoelastic properties was caused by differences in the network structure. More pendant chain ends may have been present in the network, obtained from the low molar mass copolymer precursor because of lower \bar{f} . Because the viscosity of the copolymer was higher and, there-

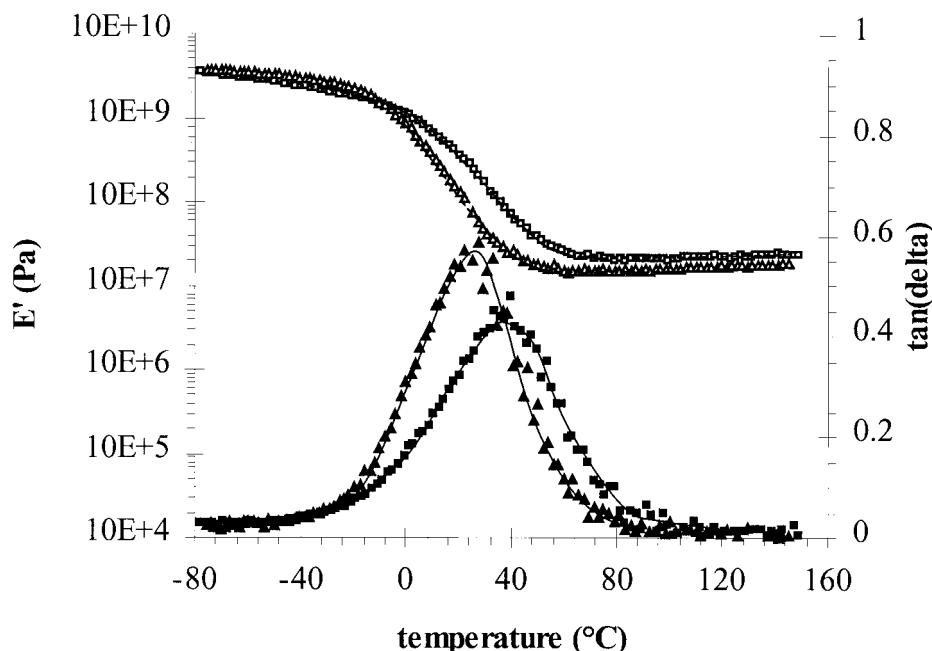


Figure 6 _ Viscoelastic properties of photocured films formed from acrylic acrylate copolymer precursors with different molar masses ($\bar{M}_c \approx 1500$ g/mol; BA/MMA/GMA = 75/14/11 mol %). The open symbols are related to E' , and the filled symbols are related to $\tan \delta$: $\bar{M}_n \approx (\triangle)$ 6200 and (\blacksquare) 30000 g/mol.

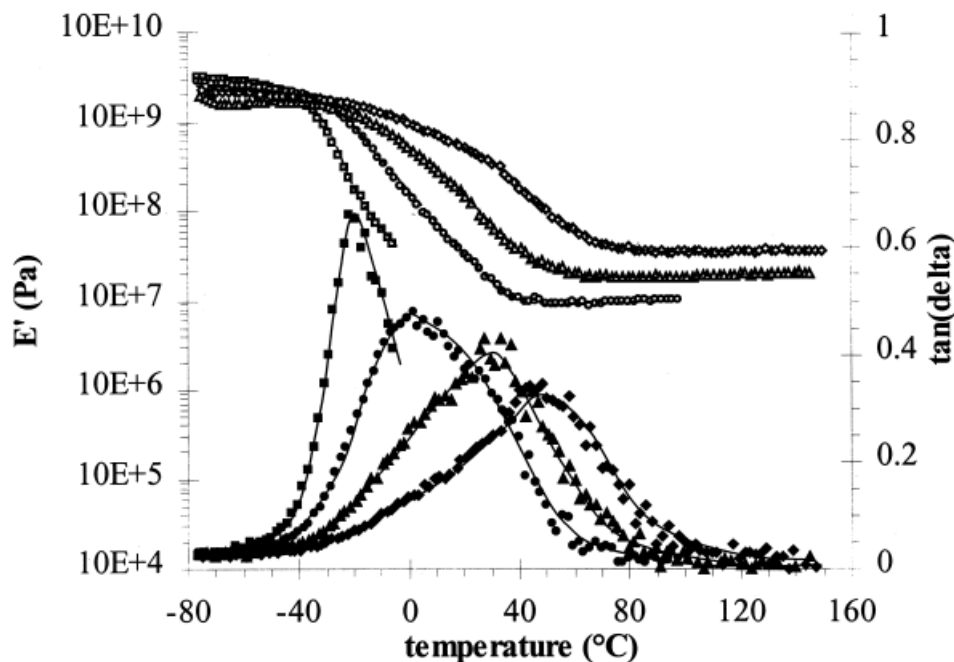


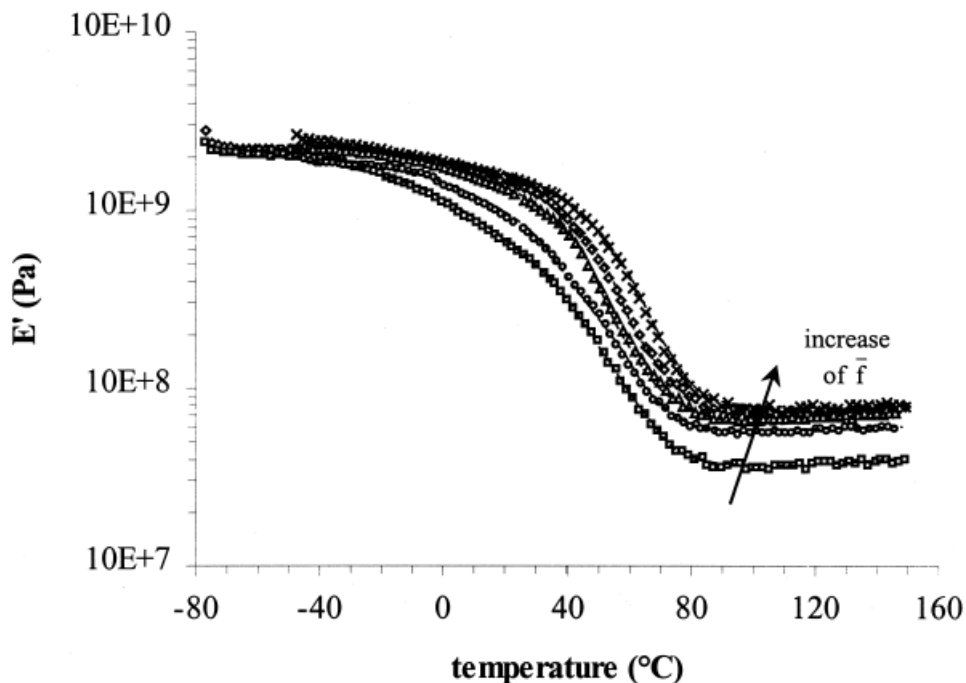
Figure 7 Viscoelastic properties of photocured films formed from acrylic acrylate copolymer precursors with different \bar{f} s ($\bar{M}_n \approx 7500$ g/mol). The open symbols are related to E' , and the filled symbols are related to $\tan \delta$: (■□) 95/5, and $\bar{f} = 2.0$, (●○) BA/GMA = 90/10 and $\bar{f} = 4.5$, (▲△) BA/GMA = 85/15, and $\bar{f} = 6.5$, (◆◇) BA/GMA = 80/20 and $\bar{f} = 8.6$.

fore, chain mobility was lower, the high molar mass copolymer precursor may have also favored intrachain crosslinking, creating very densely crosslinked regions, usually called *microgels*,^{14,28} which could also changed viscoelastic properties.

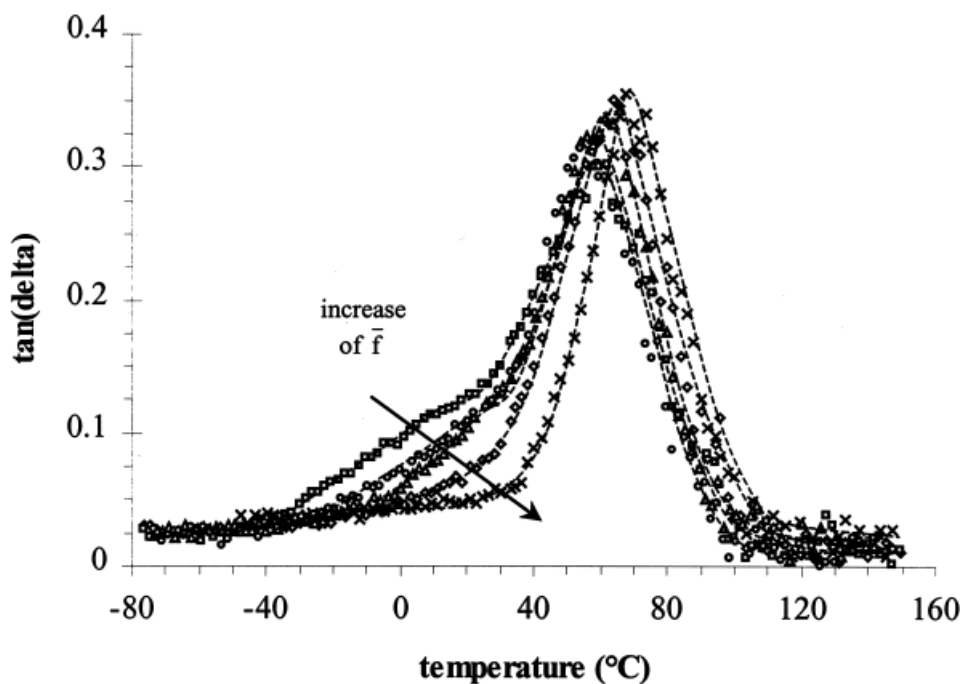
To complete the DSC study on the functionality effect, we formed photocured films from the acrylic acrylate copolymers based on BA/GMA precursors (with compositions in the range 95/5 to 80/20), with \bar{f} ranging from 2 to 8.6 and with $\bar{M}_n \approx 7800$ g/mol. Final conversion measured by ATR-IR was around 95 to 80% when \bar{f} increased. The viscoelastic properties are displayed in Figure 7. According to the previous DSC study, variation of \bar{f} of the copolymer chain greatly affected viscoelastic properties of films. T_α changed from -21 to 44°C when \bar{f} increased from 2 to 8.6. The shift of the maximum of $\tan \delta$ toward high temperatures reflected lower chain mobility into the network. The width of the $\tan \delta$ peak became much larger for films formed from high-functionality acrylic acrylate copolymer precursors. It confirmed the heterogeneous structure of networks, resulting from highly functional copolymer precursors. E'_c increased with \bar{f} of the copolymers. Film formed from the copolymer with $\bar{f} = 2$ was very brittle, and it always broke before the rubbery plateau. E'_c increased from 9.5 to 35 MPa when \bar{f} changed from 4.5 to 8.6. The enhancement of E'_c was explained by the increase in the crosslinking density and by the change in the network structure, especially the decrease of the fraction of dangling chain ends when \bar{f} increased.

Formulated acrylic acrylate copolymers

Finally, 30 wt % acrylic acrylate copolymer precursors (based on BA/GMA with compositions in the range 95/5 to 80/20) were blended in a diacrylate reactive diluent, NPGPODA. Solutions were translucent and homogeneous. No phase separation was observed even when solutions were kept at 4°C . Photopolymerized films were optically homogeneous and transparent. Conversion measured by ATR-IR was about 90% for all films. The viscoelastic properties of films with incorporation of acrylic acrylate copolymer precursors with different functionalities are shown in Figure 8. Elastic moduli of the different films are displayed in Figure 8(a). E'_c of mixtures was always lower than the one of neat NPGPODA ($E'_c = 78$ MPa). Average molar mass per crosslink was indeed lower for neat NPGPODA, leading to a more compact network. E'_c of blends increased with the \bar{f} of acrylic acrylate copolymer precursors from 36 MPa for $\bar{f} = 2$ to 70 MPa for $\bar{f} = 8.6$. The increase of E'_c was very important between $\bar{f} = 2$ and 4.5 (an increase of 21 MPa), whereas E'_c was almost constant with $\bar{f} = 6.5$ and 8.6. This confirmed the previous results that network structure probably changed when copolymer precursors with higher functionality were crosslinked. As shown in Figure 8(b), the viscoelastic transition was greatly broadened when copolymer precursors with low \bar{f} were blended with NPGPODA. This is due to the relaxation of different chains species in the network. A second relaxation was present at low temperature on the $\tan \delta$



(a)



(b)

Figure 8 Viscoelastic properties of photocured films formed from blends of NPGPODA and 30 wt % acrylic acrylate copolymer precursors with \bar{f}_S ($M_n \approx 7500$ g/mol): (a) E' as a function of temperature and (b) $\tan \delta$ as a function of temperature. (\square) $\bar{f} = 2.0$, (\circ) $\bar{f} = 4.5$, (\triangle) $\bar{f} = 6.5$, (\diamond) $\bar{f} = 8.6$, and (\times) neat NPGPODA.

curve. Such a behavior with two distinct transitions has been reported by Kannurpatti and Bowman for dimethacrylate networks²⁹ and by Barbeau et al. for PUA networks.¹⁴ In our case, the higher the copolymer functionality was, the lower the amplitude of the

second relaxation was. It eventually almost disappeared for the blend with the acrylic acrylate copolymer precursor with $\bar{f} = 8.6$. The low temperature transition probably corresponded to chains with higher mobility, such as dangling chain ends. Al-

though the width of the peak was much larger when copolymer precursors were incorporated, T_{α} was only slightly modified by the incorporation of acrylic acrylate polymers, ranging from 58 to 68°C.

CONCLUSIONS

The characterization of different acrylic copolymers, BA/GMA and BA/MMA/GMA, with different molar masses and compositions showed that T_g and the viscosity were greatly affected by both the molar mass and composition of the copolymers. We analyzed microstructure by ^1H - and ^{13}C -NMR, in particular to point out the influence of the termination reaction during radical synthesis and to confirm the random distribution of GMA units along the copolymer chains.

We chemically modified acrylic copolymers by reacting AA with the epoxy groups incorporated along the copolymer chains by the GMA units. Acrylic acrylate copolymer precursors with various molar masses and with f_s were obtained.

Crosslinking reaction of those copolymers were characterized by nonisothermal DSC. We finally cured films under UV radiation by crosslinking neat acrylic acrylate copolymer precursors or mixtures of these copolymers and a diacrylate reactive diluent. Viscoelastic properties of films were characterized by DMA. Average molar mass between crosslinks and pendant chain ends were found to be very influential parameters. Network structure changed as f of the copolymer was modified. Numerous dangling chain ends were present when f of acrylic acrylate copolymer was low. Highly crosslinked microgel-like heterogeneities were probably present in the network when high-functionality polymers were photocured.

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References

- Iwakura, Y.; Kurosaki, T.; Ariga, N.; Ito, T. *Makromol Chem* 1966, 97, 128.
- Paul, S.; Ranby, B. *J Polym Sci Part A: Polym Chem* 1976, 14, 2449.
- Kala, J.; Svec, F.; Marousek, V. *J Polym Sci Polym Symp* 1974, 47, 155.
- Gluckman, M. S.; Kampf, M. J.; O'Brien, J. L.; Fox, T. G.; Graham, R. K. *J Polym Sci* 1959, 37, 411.
- Nordstrom, J. D.; Hinsch, J. E. *Ind Eng Chem Prod Res Dev* 1970, 9, 155.
- Nair, C. P. R. *Angew Makromol Chem* 1993, 212, 53.
- Uminski, M.; Saija, L. M. *Surf Coat Int* 1995, 6, 244.
- Kloosterboer, J. G. *Adv Polym Sci* 1988, 84, 1.
- Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Macromolecules* 1994, 27, 650.
- Anseth, K. S.; Anderson, K. J.; Bowman, C. N. *Macromol Chem Phys* 1996, 197, 833.
- Kannurpatti, A. R.; Anderson, K. J.; Anseth, J. W.; Bowman, C. N. *J Polym Sci Part B: Polym Phys* 1997, 35, 2297.
- Dusek, K.; Galina, H.; Mikes, J. *Polym Bull* 1980, 3, 19.
- Dusek, K. *Angew Makromol Chem* 1996, 240, 1.
- Barbeau, P.; Gerard, J.-F.; Magny, B.; Pascault, J.-P.; Vigier, G. *J Polym Sci Part B: Polym Phys* 1999, 37, 919.
- Le Blainvaux, F.; Madec, P.-J.; Marechal, E. *Polym Bull* 1985, 13, 237.
- Brandrup, J.; Immergut, E. H.; Eds. *Polymer Handbook*, 3rd ed. Wiley: New York, 1989; p II/298, 299.
- Pham, Q. T.; Petiaud, R.; Waton, H.; Llauro-Darricades, M.-F. *Proton and Carbon NMR Spectra of Polymers*; Penton: London, 1991.
- Hild, G.; Lamps, J. P.; Rempp, P. *Polymer* 1993, 34, 2875.
- DiBenedetto, A. T.; DiLandro, L. *J Polym Sci Part B: Polym Phys* 1989, 27, 1405.
- Lin, Y. H. *Makromol Chem Macromol Symp*, 1992, 56, 1.
- Lin, Y. H.; Juang, J. U. *Macromolecules* 1999, 32, 181.
- Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J Polym Sci Part B: Polym Phys* 1999, 37, 1023.
- Weill, A. In *Techniques de L'ingénieur M. Chatain, Ed.*; AM3. 1981, p A3615-12.
- Soundararajan, S.; Reddy, B.S.R.; Rajadurai, S. *Polymer* 1990, 31, 366.
- Dietz, J. E.; Peppas, N. A. *Polymer* 1997, 38, 3767.
- Kloosterboer, J. G.; Van de Hei, G. M. M.; Gossink, R. G.; Dortant, G. C. M. *Polym Commun* 1984, 25, 322.
- Kannurpatti, A. R.; Anseth, J. W.; Bowman, C. N. *Polymer* 1998, 39, 2507.
- Chiu, Y. Y.; Lee, L. J. *J Polym Sci Part A: Polym Chem* 1995, 33, 257.
- Kannurpatti, A. R.; Bowman, C. N. *Macromolecules* 1998, 31, 3311.