Preparation and Glass Transition Temperature of Hyperbranched Poly[Allyl Methyl Maleate-*co*-*N*-Propyl Maleimide]

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ABSTRACT: The kinetics and molecular weight averages of the hyperbranched polymers formed by the alternating copolymerization of equimolar allyl methyl maleate (AMM) and *N*-n-propyl maleimide (PMI) were investigated. The yields, molecular weight averages, and polydispersity indices as well as the branching degrees of the produced copolymers increased with increasing initiator concentrations and prolonged polymerization time. The trends of the experimental molecular weights as determined by size exclusion chromatography were in good agreement with the theoretical predictions. The molecular weight distribution indices fit the curve given by $M_w/M_n = 1/(1\text{-}x_D)$, and the molecular weights fit the curve given by $M_w = 4076/(1\text{-}x_D)^2$, where x_D was the conversion of vinyl groups. DSC studies demonstrated a nonlinear relation of T_g values to the reciprocal of molecular weight (M), and T_g values decreased with the increase of molecular weight. For the T_g values of highly branched polymers in high molecular weight range, a relation of $T_g = T^0_{g\infty} + k/M$ was obtained, where $T^0_{g\infty}$ was obtained by extrapolating to infinite molecular weight and k was a constant. $T^0_{g\infty}$ was 136°C, and k = 2.9 for this work. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1941–1947, 2005

Key words: allyl methyl maleate; glass transition temperature; hyperbranched polymers; propyl maleimide

INTRODUCTION

The synthesis of hyperbranched polymers has received much interest in the past decades. The primary reason is that these highly branched polymers often have significantly different physical properties from their linear analogues, for example, the glass transition properties of high interest. For a branched polymer compared with a linear polymer of the same molecular weight, the additional number of chain ends in the branched molecule will decrease glass transition temperature (T_g), while the restriction in mobility caused by the junction point will increase T_g.[1–3] The nature of the chain ends dramatically affects the glass transition temperature of dendritic macromolecules, with increases in T_g following increases in chain-end polarities.[2] Thus, it is possible that hyperbranched polymers have much lower glass temperatures than their linear counterparts, and the hyperbranched polymers with higher molecular weights may have lower glass temperatures.[4]

In the course of developing methods for the synthesis of hyperbranched polymers, we have come to the conclusion that electron donor-acceptor monomers are very versatile building blocks for the direct synthesis of such polymers. In our previous articles, we have described a unique approach for the production of AB type of hyperbranched copolymers[5] by free radical alternating copolymerization of an AB (allyloxy maleic acid) or AA (diallyl ether)/B′ (maleic anhydride) system.[6,7] In this work we wanted to explore the possibility of replacing maleic anhydride with maleimide in this type of alternating copolymerization approach to hyperbranched polymers. Our interest in maleimide polymers stemmed from the fact that they normally exhibit excellent thermal stability, chemical resistance, and mechanical properties. As a consequence of this, maleimide polymers are utilized in very demanding applications, for example, in the aerospace industry, in the production of high-tech composites, and so forth. In addition, maleimide resins (usually bismaleimide compounds) are often cured by allyl chemicals for the purpose of improving toughness, and the modification of bismaleimide resin by allyl compounds seems to be one of the major development directions for this family of polymers.[8] Like maleic anhydride, maleimides also belong to the group of

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strong electron acceptor monomers. According to literature, many free radical copolymerization systems of styrene and *N*-phenyl maleimides formed alternating copolymers over a wide range of monomer feeds.[9] Studies of the reactions between maleimide and allyl compounds also indicate that the alternating mechanism in copolymerization is prevailing; however, maleimide homopolymerization could be detected at temperatures above 200°C.[10]

The aim of the present work was to extend the range of hyperbranched polymers produced by the aforementioned free radical copolymerization approach towards novel maleimide polymers and to investigate its properties. We report the preparation of hyperbranched polymers through alternating free-radical copolymerization of allyloxy methyl maleate (AMM) with *N*-n-propyl maleimide (PMI). Thermal properties of these copolymers were also studied by differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

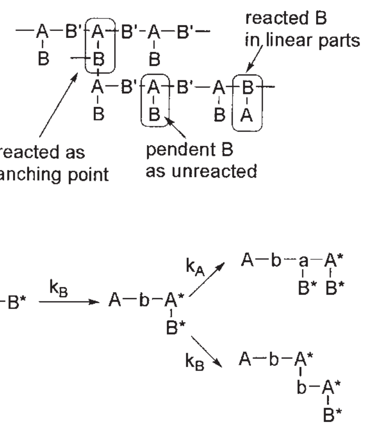
All solvents used were analytical grade. Benzoyl peroxide (BPO; Fluka) was recrystallized from a tetrahydrofuran (THF) solution. *N*-n-propyl maleimide (PMI) and allyl methyl maleate (AMM) were synthesized according to refs. 11 and 12, respectively. Their structures and purities were determined by ^{1}H, and gas chromatography-mass spectrometry (GC-MS).

Polymerization procedure

The copolymerization of equimolar PMI with AMM was carried out in 5-mL sealed ampoules at 50°C with dry THF as the solvent (50 wt %) and BPO as the radical initiator. The unit of BPO concentration used in this paper is mole percentage of all vinyl groups in the reaction mixtures. The produced poly(AMM-*co*-PMI)s were purified by precipitating in diethyl ether/dissolving in dichloromethane four cycles to remove unreacted monomers, and subsequently dried in vacuum. The polymers were obtained as white brittle solids. Yield of polymers was calculated as the fraction of the weight of the polymer to that of the starting reagents. Conversion of total double bonds was measured by ^{1}H NMR.

Polymer characterization

The ^{1}H NMR spectra were recorded in dimethylsulfoxide-d_6 (DMSO-d_6) relative to DMSO-d_6 (2.50 ppm) on a Bruker AC-250 spectrometer at room temperature. The molecular weights of the polymers were measured by a size-exclusion chromatograph (SEC) using a 2142 differential refractometer manufactured by Pharmacia. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC 7 thermal analyzer. About 7.5 (±0.5) mg of the polymer sample was crimped in an aluminum pan and heated at a rate of 10°C/min from 50 to 280°C in a nitrogen atmosphere.



Scheme 1

RESULTS AND DISCUSSION

Copolymerization of *N*-n-propyl maleimide (PMI) and allyl methyl maleate (AMM)

The copolymerization of AMM and PMI and the structural characteristics of the obtained branched polymers are illustrated in Scheme 1. A denotes the allyl group of AMM, B the maleate group of AMM, and B′ represents the PMI monomer. According to literature, homopolymerization of PMI could be omitted, especially at low temperature of 50°C, although dimerization might occur through combination termination. Alternating copolymerization between allyl and maleimide groups forms linear chains with pendant unsaturated maleate groups. Copolymerization starting from the pendant maleate groups by any method, such as attack by initiator radical or chain transfer, causes branching. Thus, highly branched polymers with both allyl and maleate end groups will be obtained.

The results of free radical copolymerization of AMM and PMI at 50°C are shown in Table I. The dependence of the copolymer yield to initiator concentration at different reaction times is illustrated in Figure 1. It is manifested in Figure 1 that both longer reaction times and higher initiator concentrations improved significantly the yields obtained for copolymerization of equivalent molar ratios of PMI and AMM.

The SEC investigation of the polymers revealed some interesting features. In the system at polymerization time of 24 h and temperature of 50°C, the weight average molecular weights (M_w) and their dis-

TABLE I
Characteristics of Copolymer of AMM and PMI Formed in THF at 50°C. BPO Was Used as Free Radical Initiator.

Entry no.	BPO/% mol	Time/h	Yield/wt %	conversion/%	M_w	M_w/M_n	T_g/°C
1	0.36	24	25	24	12,800	1.6	179
3	0.89	24	29	27	13,000	1.6	174
5	1.34	24	35	33	13,400	1.8	168
7	1.97	24	49	46	14,200	1.8	159
9	2.50	24	52	49	15,000	2.1	155
2	0.39	48	44	42	13,000	1.8	170
4	0.84	48	49	46	13,400	1.8	158
6	1.36	48	53	49	16,000	2.0	154
8	1.99	48	62	59	20,000	2.5	149
10	2.50	48	68	64	30,000	3.6	147

tribution indices (M_w/M_n) were found to increase slowly as the concentration of BPO increased (Figs. 2 and 3); whereas, in the case of prolonged polymerization times exceeding 24 h and keeping all other parameters constant, a general trend toward a significant increase of M_w and M_w/M_n values as a function of increasing BPO concentrations was clearly perceptible. In addition, it could be noted that the polymerization systems with higher BPO concentrations were more sensitive to reaction time. Thus, at longer reaction time, higher BPO concentrations afforded faster increase of both molecular weight and molecular weight distribution indices. The M_w and M_w/M_n of the polymers formed with BPO concentration less than 1 mol % kept nearly unchanged after 24 h of copolymerization. This might indicate a threshold initiator concentration for branching to take place. This observation was in line with our previous studies that have shown that a prerequisite for the formation of hyperbranched structures was high initial initiator concentration. Increased initiator concentrations may increase the reaction rate and branching probability, and consequently increase the molecular weight of the formed polymer. The copolymerization processes involve incorporation of large macromolecules with vinyl groups or macromolecular radical intermediates formed early in the polymerization into a vinyl polymer to afford an irregularly branched polymer. Hence, molecular weight could nonlinearly increase with reaction time.

The theoretical evaluation of molecular weight with conversion of the double bonds for the self-condensing vinyl polymerization (SCVP)[13] has been carried out by Müller and coworkers.[14] According to Müller's work,

$$M_w \approx \frac{m_M}{(1 - x_D)^2} \tag{1}$$

$$\frac{M_w}{M_n} \approx \frac{1}{1 - x_D} \tag{2}$$

where x_D is the conversion of double bonds, and m_M is the molecular weight of repeating units. The alternating copolymerization system in this study is comparable with Müller's system where eqs. (1) and (2) were obtained, because the -AB- or -AB′- can be regarded as one repeating unit and branching is by way of pendent B groups.

To compare with the theoretical prediction, the molecular weight and the polydispersity indices in Table I were plotted against the conversion of double bonds. The data of different reaction time and different initiator concentration in the plots seemed to follow a certain trend-line, which was in accord to eqs. (1) and

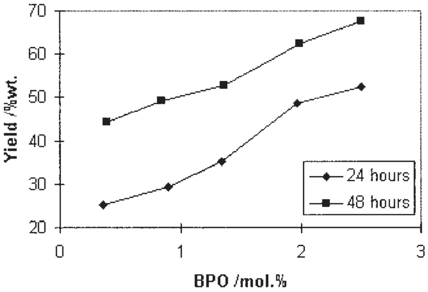


Figure 1 Relation of the polymer yield to initiator concentrations.

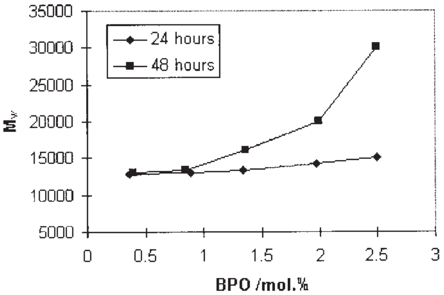


Figure 2 Dependence of weight average molecular weights on initiator concentrations.

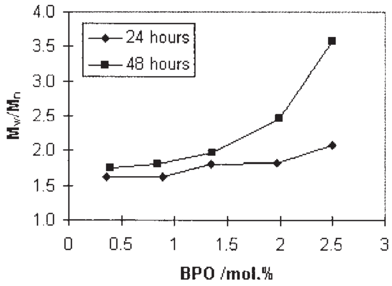


Figure 3 Dependence of molecular weight distribution on initiator concentrations.

(2). The M_w/M_n-conversion curve in the middle conversion part (obtained from 48 h mainly) fit the theoretical curve by $1/(1-x_D)$ very well (Fig. 4). The polydispersity index in the higher conversion was higher than predicted probably because of condensation between macromolecules. The high conversion part of the M_w-conversion curve could be fitted by the theoretical curve of $4076/(1-x_D)^2$ (Fig. 5). The value of 4076 is equal to the molar mass of about 13 repeating units of (AMM-PMI), which might be due to formation of linear segments. The formation of linear chains could also account for the platforms in Figures 2–5, plotted according to the data obtained from reactions in 24 h.

^{1}H NMR studies

The degree of branching (DB) is one of the most important parameters to describe the features of hyperbranched polymers. So far two techniques are generally used to determine the degree of branching of hyperbranched polymers: the first is based on NMR measurements of different building units[15] and the second method on degradation of hyperbranched backbones.[16] The former method is limited to polymers exhibiting differences in NMR resonance, and the latter is only applicable to those fully degradable polymers. Neither of the two techniques are applicable to the measurement of DB of poly[allyl methyl maleate-*co*-*N*-propyl maleimide]. However, the extent of branching can be discussed in terms of the branching probability instead of measuring the DB directly. The branching probability was defined as the molar fraction of branch junctions to all repeating units.

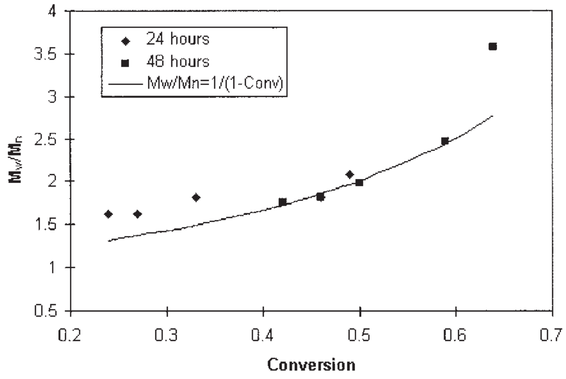


Figure 4 Relation of M_w/M_n to conversion of double bonds.

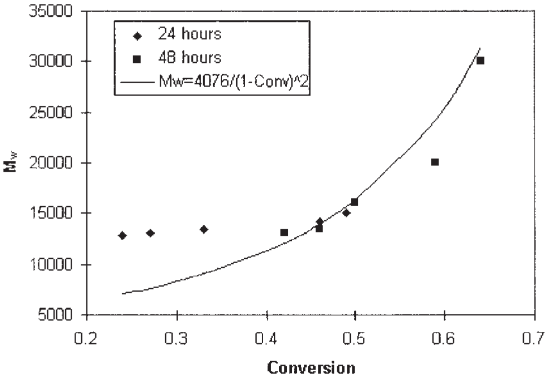


Figure 5 Relation of M_w to conversion of double bonds.

For simplicity, the copolymerization of AMM and PMI was outlined for an AB/B′ system. Let A denote the allyl group of AMM, B the maleate group of AMM, and B′ represent the PMI monomer. Branching is assumed to occur by propagating from pendent B groups. Values m_B, $m_{B'}$, and m_A denote the molar concentrations of respective polymerized components in the hyperbranched polymers. Reacted B in the hyperbranched structure can exist either as part of the linear chain (m_{Bl}) or as branch junctions (m_{Bb}); thus, $m_B = m_{Bl} + m_{Bb}$. We defined a branching probability ρ, as the molar ratio of polymerized B at branching junctions (m_{Bb}) to all B units in a macromolecule. The latter is equal to A, and therefore ρ can be expressed as:

$$\rho = m_{Bb}/m_A \tag{3}$$

Presuming that only alternating copolymerization takes place, we can form the following eq. (4):

$$m_A = m_B + m_B \tag{4}$$

Thus,

$$\rho = 1 - \frac{m_{B'}}{m_A} - \frac{m_{Bl}}{m_A} \tag{5}$$

According to eq. (5), the compositions of A and B′ are related to the branching probability, ρ, if m_{Bl} can be distinguished.

The degree of branching (DB) was defined by Fréchet and coworkers,[17]

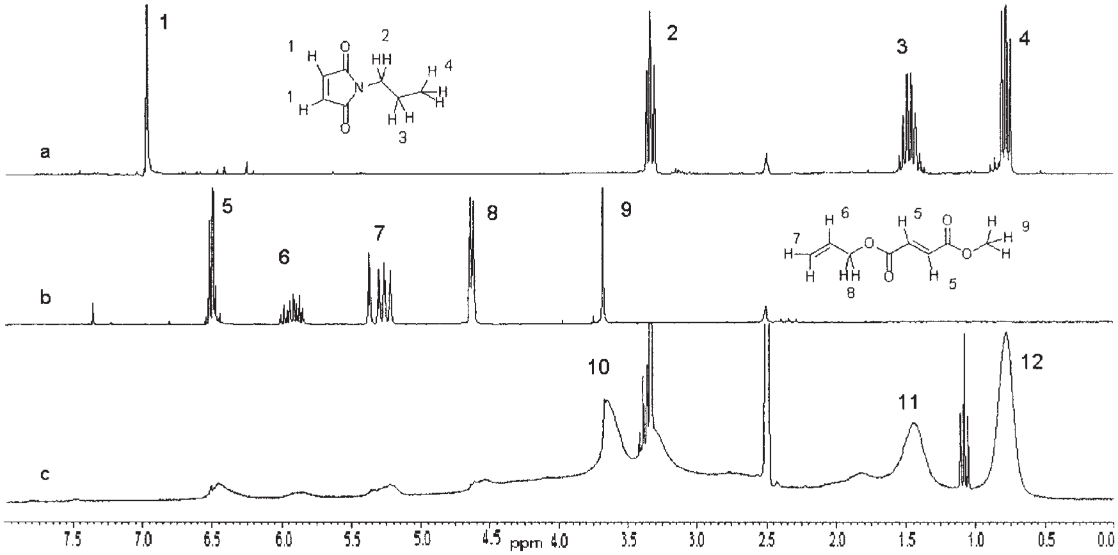


Figure 6 ^{1}H NMR spectra of (a) PMI, (b) AMM, and (c) polymer entry 10 in Table I.

$$\mathrm{DB} = \frac{\text{dendritic units} + \text{terminal units}}{\text{dendritic units} + \text{terminal units} + \text{linear units}} \tag{6}$$

$$= \frac{m_{\mathrm{Bb}} + m_{\mathrm{terminal}}}{m_{\mathrm{A}}} = \rho + \frac{m_{\mathrm{terminal}}}{m_{\mathrm{A}}} \tag{7}$$

where m_{terminal} is the molar concentration of all terminal units. Thus, the branching probability of pendent B can be used to characterize the DB.

A typical ^{1}H NMR spectrum of the polymers is shown in Figure 6c together with spectra of the starting monomers AMM and PIM. Peak 10 arose from proton 9 of methyl groups of AMM, and peaks 11 and 12 from protons 3 and 4 of the propyl group of PMI, respectively. From Figure 6, we measured the ratios of peak 10 to peak 11 or to peak 12 for the polymers, which correspond to $m_A/m_{B'}$ in eq. (5). The change of the integration ratios as a function of BPO concentrations is illustrated in Figure 7. The ratios of all the polymers from reactions of 48 h with BPO concentrations less than 1.35 mol % remained nearly constant within experimental error, and increased with the increase of initiator concentration at higher initiator concentrations. Hence, the branching degrees of the obtained polymers were increased with higher reaction times and increased initiator concentrations. The platforms were regarded as results from prevailing linear polymers.

DSC studies

The glass temperature (T_g) of polymers is one of the general material properties of both theoretical and practical interest. Molecular weight,[18,19] entanglements, and chain-end composition[20] have been revealed to affect T_g. The dependence of T_g on molecular weight (M) can be described by the Fox–Flory equation as

$$T_g = T_{g\infty} - k/M \tag{8}$$

where $T_{g\infty}$ is the value of T_g at infinite molecular weight and k is a constant. A theoretical interpretation of eq. (8) on the free volume theory contributed the dependence of T_g on the reciprocal of molecular weight to the effects of chain ends, that is, the free volume fraction of chain ends increases with decreased molecular weight. However, the plots of T_g versus the reciprocal of molecular weight were often two or more intersecting straight lines.[20,21] The increased elevation of dependence of T_g on molecular weight was suggested to be due to an increasing concentration of entanglements.[20]

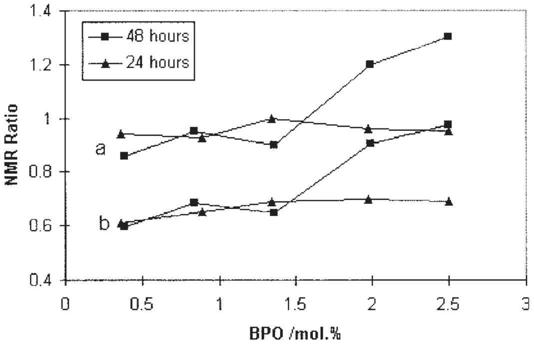


Figure 7 Relation of the integration ratios of NMR spectra to initiator concentrations: (a) integration ratio of peak 10 to peak 11, (b) peak 10 to peak 12 (see Fig. 6).

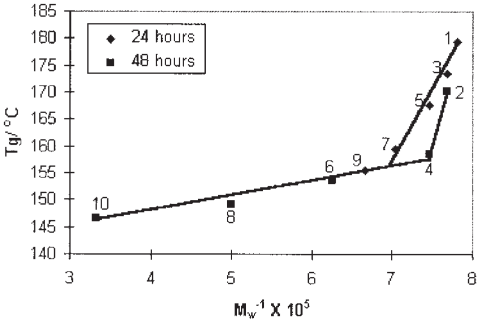


Figure 8 Dependence of glass temperatures on molecular weights. The numbers on the figure are according to the entry numbers in Table I.

The glass transition temperature of crosslinked, uncrosslinked,[22] or dendritic polymers[3] was recently treated theoretically by Stutz. It was concluded that the glass transition temperature was a function of the backbone glass temperature (structure-dependent), the amount of end-groups, and the amount of crosslinks or branch points. The end groups and branching sites affect the glass temperature in opposite directions. The end groups decrease the glass temperature but branching increases it.

Wooley and coworkers also studied the variation of T_g with molecular weight and chain-end composition for dendritic polyethers and polyesters.[2] The nature of the chain ends dramatically affects the glass transition temperature of dendritic macromolecules, with increases in T_g following increases in chain-end polarities. Kim also pointed out the T_gs of the polymers were greatly affected by the terminal functional groups.[1]

We studied the thermal properties of the copolymers by DSC. The T_g values showed significant shifting to lower temperatures along with increased initiator concentration, from 180 to 150°C for the polymer obtained in 24 h, and from 170 to 140°C for those obtained in 48 h. The compositions of linear segments of chains/branches in all the polymers under investigation were statistically the same, except for possible differences in branching extent.

The T_g values versus the reciprocal of molecular weight were presented by intersecting straight lines (Fig. 8). For the linear or lowly branched polymers (entries 1, 3, 5, and 7, and 2 and 4), the T_g values decrease rapidly with increasing molecular weight. At higher molecular weights of branched polymers, the dependence of T_g on the M^{-1} turned to a new straight line with a gentle slope. For the polymers formed in 48 h, the two lines intersected at lower molecular weight than those in 24 h. Most significant in Figure 8 was that the dependence of T_g on the reciprocal of molecular weight was anti-Fox–Flory type, that is, the T_g values increased with the bigger reciprocal of molecular weight. This can be rationally interpreted by the variation of the number of chain ends. The Fox–Flory equation actually implies that the number, hence the free volume fraction, of chain ends increases with decreased molecular weight. However, the increment of chain ends with the increase of molecular weight in the case of highly branched structures is much more significant than that with a reduction of molecular weight in linear polymers. Thus, the T_g values of dendritic polymers showed reversing dependence on the reciprocal of molecular weight compared with the Fox–Flory type relation of linear polymers.

For highly branched polymers in high molecular weight range, we obtained from Figure 8

$$T_g = T^0_{g\infty} + k/M \qquad (9)$$

where $T^0_{g\infty}$ was obtained by extrapolating to infinite molecular weight and k is a constant. $T^0_{g\infty}$ seems the T_g of a highly branched polymer at infinite molecular weight. The plus sign before the reciprocal of the molecular weight in eq. (9) results from the reversing dependence of the free volume fraction of chain ends in a dendritic polymer on molecular weight, compared with eq. (8) for linear polymers. From Figure 8, we obtain $T^0_{g\infty}$ as 136°C and $k = 2.9$.

Though there were two different intersections found for the polymers obtained at different reaction time, the two intersections were correspondent to the same conversion of about 0.4. From Figures 4 and 5, the trends of the experimental molecular weights obtained by conversion above 0.4 were in good agreement with the theoretical predictions. If the T_g data were plotted against conversion of double bonds, the T_g values showed a nearly linear reduction with increased conversion (Fig. 9). Figure 9 combined with the aforementioned figures suggested that high conversion is essential for the formation of highly branched structures. The minimum conversion to ensure the formation of highly branched structures seemed to be 0.4 from Figures 4 and 5, and 7 and 8.

Caution should be taken that the glass temperature of dendritic polymers is also strongly affected by the

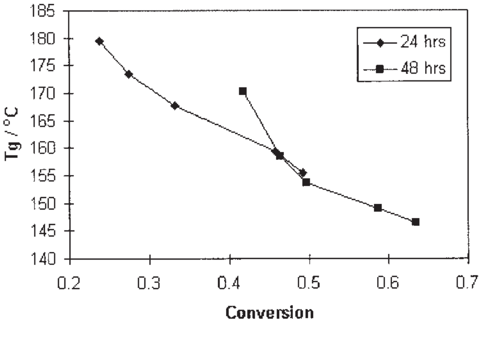


Figure 9 Relation of glass temperatures to conversion of double bonds.

nature of end-groups, for example, the polarity, as aforementioned. It was well documented in the literature that *N*-aryl substituted maleimides units can increase T_g of the copolymers (see, for example, refs. 8 and 23). Thus, by varying the nitrogen substituted groups, a variety of dendritic macromolecules may be prepared covering a wide range of glass transition temperatures.

The transition in the relations of T_g to molecular weight is typical for linear polymers. The molecular weight at an intersection was defined as a critical molecular weight, M_g. An increased elevation of T_g at molecular weight greater than M_g is due to an increasing concentration of entanglements.[20] This kind of transition was also observed in the relation of T_g to the molecular weight of dendrimers; however, it could not be interpreted by entanglement behavior.[21] Very recently, we found a reverse and nonlinear relation between T_g and molecular weight for hyperbranched polymers in a comparison to linear polymers based on chain-end free volume theory.[24] The transition and anti-Fox–Flory behaviors observed in the relation of T_g to molecular weight of hyperbranched polymers in this work can be well interpreted by such a nonlinear relation.

CONCLUSIONS

High initiator concentration and long reaction time were required to afford highly branched structures from the copolymerization of allyl methyl maleate and *N*-n-propyl maleimide. For these polymers obtained from reactions for 48 h, the molecular weight distribution indices fit curve $M_w/M_n = 1/(1\text{-}x_D)$, and the molecular weight fit $M_w = 4076/(1\text{-}x_D)$,[2] where x_D is the conversion of double bonds. DSC studies demonstrated that T_g values showed anti-Fox–Flory type dependence on the reciprocal of the molecular weight, that is, $T_g = T^0_{g\infty} + k/M$, where $T^0_{g\infty}$ was the T_g value of a highly branched polymer at infinite molecular weight and k is a constant. $T^0_{g\infty}$ was obtained as 136°C, and k = 2.9 for the systems in this study. This might be because the free volume fraction of chain ends of dendritic polymers increased with molecular weight. Combined analysis of kinetics, NMR, and DSC studies suggested that high conversion was essential for the formation of highly branched structures, and the minimum conversion to ensure the formation of highly branched structures seemed to be 0.4.

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