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Glass transition temperature of crosslinked poly(ether sulfone)s

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A series of crosslinkable maleimide-ended poly(ether sulfone)s has been prepared using a range of molecular masses. The effect of the crosslinking reaction on the glass transition temperatures (T_gs) is observed. In the range of molecular masses studied, the T_gs after crosslinking are predominantly dependent on the intrinsic nature of the polymer and are not dependent on the final crosslink density. However, T_gs of partially crosslinked polymers are related to the concentration of chain-ends consumed by the crosslinking reaction.

(Keywords: poly(ether sulfone); glass transition temperature; maleimide crosslinking)

INTRODUCTION

The glass transition is the most important and best studied transition in synthetic polymers. The relationships between molecular mass and glass transition temperature (T_g) for linear polymers are well established[1–3]. It is well known that the temperature of glass transition is an increasing function of the molecular mass for a linear polymer. However, above a critical value of molecular mass, constant T_g values are sometimes reported. This value of molecular mass corresponds roughly to the critical molecular mass (M_{cr}) found in melt viscosity experiments and is related to the number-average molecular mass between entanglements (M_e)[4,5].

In crosslinked systems the situation is much more complicated. It is generally assumed that in crosslinked polymers the T_g is a function of the crosslink density. Theoretical and empirical relations involve linear dependencies, but exponential or logarithmic relationships can also be found[6–8]. However, regarding structural and chemical aspects, two kinds of crosslinking can be distinguished. The first corresponds to networks obtained by a post-synthesis crosslinking. This family can be subdivided into two classes depending on the location of the crosslinking site. The polymer can be crosslinked along the backbone of the chain or specifically at chain-ends. The second family corresponds to networks obtained by 'polymerization' or by 'curing' of multifunctional (i.e. average of more than two reactive functionalities), low molecular mass compounds (monomers or oligomers).

In this work, glass transition temperatures for maleimide-ended (ether sulfone) polymers of different molecular masses have been studied as a function of crosslinking time and crosslinking temperature. The production of insoluble species is also reported.

EXPERIMENTAL

Reagents and solvents

N-Methyl-2-pyrrolidone (NMP), for gel permeation chromatography, was a technical solvent from ISP which was refluxed over calcium hydride and distilled under reduced pressure before use.

Lithium bromide p.a. was a commercial product of Merck.

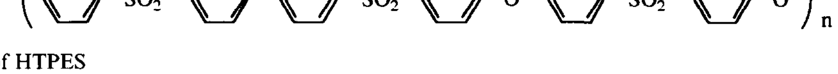
Cyclopentanone 99%, calcium hydride 93% and dimethyl-d_6 sulfoxide 99% were commercial products of Janssen.

Dichloromethane and methanol were technical solvents and were distilled before use.

Polymers

High temperature poly(ether sulfone)s. The synthesis and characterization of high temperature poly(ether sulfone) (HTPES) polymers was reported in a previous paper[9]. The repeat unit of this polymer is shown in *Scheme 1*.

Characterization of maleimide-ended polymers is



Scheme 1 Repeat units of HTPES

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reported in the present paper. Samples of maleimide-ended polymer were cured in glass vacuum cells under different conditions of temperature and time.

Poly(ether sulfone) copolymer. A fully amine-ended poly(ether sulfone) (PES) copolymer was synthesized. In this copolymer, the ratio of ether links to sulfone links is 10 : 7.

This polymer was fractionated at room temperature by batch fractionation. The polymer was dissolved in dichloromethane to obtain a dilute solution. The solution was separated into two phases by the addition of methanol as non-solvent. The partitioning of the polymer into two phases depends on molecular mass. The process was repeated until all the polymer was separated into the desired number of fractions. The amine-ended polymers obtained were functionalized by reaction with maleic anhydride. Samples of maleimide-ended polymer were cured in glass vacuum cells.

Techniques

Nuclear magnetic resonance. ^{1}H n.m.r. spectra were obtained on samples dissolved in dimethyl-d_6 sulfoxide at room temperature and were recorded on a Brucker AM500 spectrometer. Experimental conditions were: concentration $\sim 20\,\mathrm{g\,dm^{-3}}$; scan frequency 500 MHz; spectral width 8000 Hz; pulse width 15 μs; relaxation delay 2 s.

Differential scanning calorimetry. The d.s.c. heating scans were recorded on 10 mg samples of material in a Perkin-Elmer DSC 7 calibrated with indium and zinc. The scanning rate was $20^\circ\mathrm{C\,min^{-1}}$ in all cases.

Size exclusion chromatography. S.e.c. was performed using a chromatograph comprising a Millipore-Waters 600A pump, an automatic injector Millipore-Waters 712 Wisp and a set of two mixed-bed Shodex columns from Showa Denko. Analyses were carried out in NMP at room temperature. Sample concentrations were $\sim 0.2\,\mathrm{g\,dm^{-3}}$.

Insoluble fraction determination. Crosslinked samples were immersed in a refluxing solvent for two days. Cyclopentanone and dichloromethane were used for HTPES and PES copolymer samples, respectively. After filtration, the weight fraction of insoluble species was determined.

RESULTS AND DISCUSSION

Polymer characterization

HTPES polymers. Main characterizations were made on the amine-ended polymers prior to their conversion to maleimide chain-ends. Values of number-average molecular mass ($\bar{M}_n$), chain-end concentration and glass transition temperature (T_g) of nominally 'amine'-ended HTPES polymers are reported in *Table 1*.

Extrapolation of the glass transition temperature to infinite number average molecular mass was made in a former paper and a T_g of 272.5°C was obtained[9].

Table 1 Values of number-average molecular mass ($\bar{M}_n$), chain-end concentration and glass transition temperature (T_g) of nominally amine-ended HTPES polymers

Sample	$\bar{M}_n$ n.m.r. ($\mathrm{g\,mol^{-1}}$)	Chain-ended concentration n.m.r.		T_g (°C)
		% NH_2	% OH	
HTPES 1	3700	83	17	186
HTPES 2	6200	95	5	218
HTPES 3	11 700	88	12	246

Table 2 Values of number-average molecular mass ($\bar{M}_n$), weight average molecular mass ($\bar{M}_w$) and glass transition temperature (T_g) of PES copolymer samples

Sample	$\bar{M}_n$ n.m.r. ($\mathrm{g\,mol^{-1}}$)	$\bar{M}_n$ s.e.c. ($\mathrm{g\,mol^{-1}}$)	$\bar{M}_w$ s.e.c. ($\mathrm{g\,mol^{-1}}$)	T_g (°C)
Starting polymer	–	10 800	22 700	209
PES 1	28 700	29 300	38 900	216
PES 2	25 900	25 100	38 200	215
PES 3	19 200	22 100	29 300	213
PES 4	13 400	14 400	20 000	207
PES 5	11 800	12 500	15 600	206
PES 6	7200	7100	9900	195
PES 7	3700	2200	3800	167
PES 8	2100	1500	2400	–

These samples were converted to maleimide chain-ends and complete conversion of amine chain-ends was confirmed by ^{1}H n.m.r.

PES copolymers. A series of eight amine-ended polymers was obtained by fractionation. A constant ratio between ether and sulfone bonds for the eight fractions was observed by ^{1}H n.m.r. The ^{1}H n.m.r. spectrum of fraction 6 is shown in *Figure 1*.

Molecular data for these amine-ended polymers are reported in *Table 2*. Molecular masses were determined by ^{1}H n.m.r. and also by s.e.c. using a PES calibration curve[10].

Extrapolation of the glass transition temperature to infinite number-average molecular mass is reported in *Figure 2*. A T_g of 223°C is obtained.

Amine-ended fractions 1 to 6 were functionalized by reaction with maleic anhydride. For the maleimide-ended polymers, complete conversion of amine chain-ends was assessed by ^{1}H n.m.r.

Glass transition temperatures and percentages of insoluble species for crosslinked polymers

HTPES polymers. The maleimide-ended HTPES 1 was first crosslinked at different temperatures for 1 h. Glass transition temperatures were then recorded. Results are shown in *Figure 3*.

The observed linear relation between the temperature of cure, T_{cure}, and T_g for T_{cure} below 280°C is due to vitrification. During the crosslinking reaction the T_g of the system increased. When the T_g became similar to T_{cure}, the mobility of the end groups decreased strongly and the crosslinking mechanism stopped. Such behaviour has already been reported for maleimide-ended poly(ether ketone)s[11] and for styrene-terminated

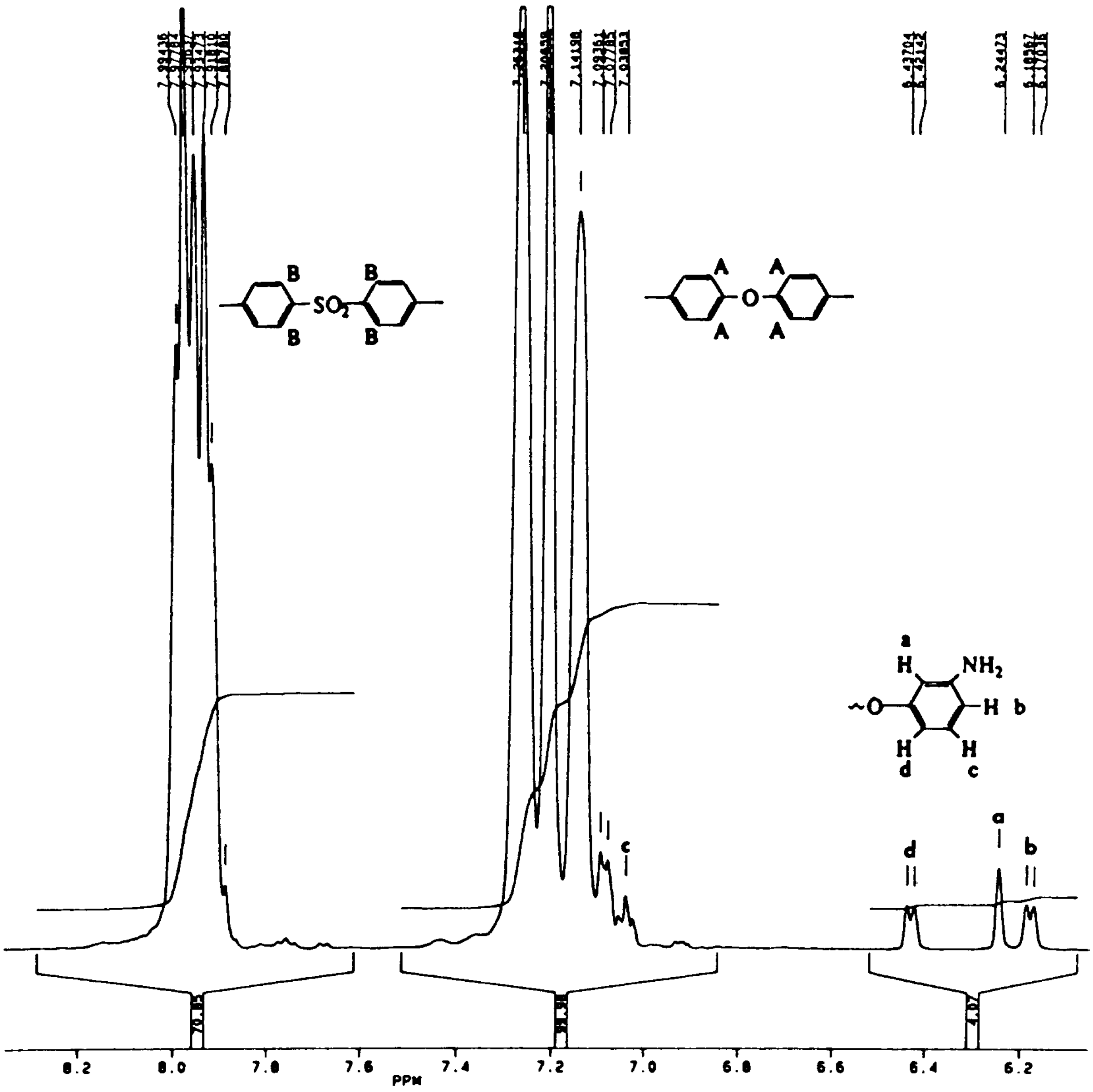

Figure 1 ^{1}H n.m.r. spectrum of the amine-ended PES 6 copolymer sample

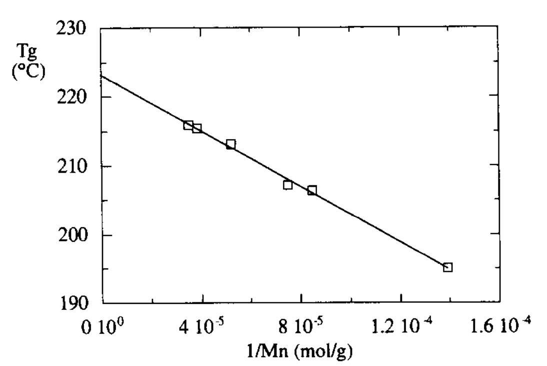

Figure 2 Extrapolation of the glass transition temperature to infinite molecular mass for PES copolymers

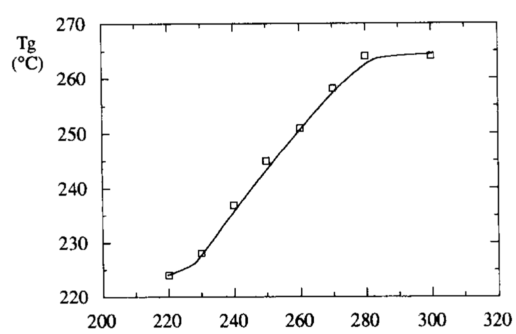

Figure 3 Glass transition temperature of HTPES 1 after 1 h of curing at different temperatures

polysulfone[12]. Takeda *et al.*[13] have also observed a dependence of the T_g values on curing temperature for very low molecular mass bismaleimide compounds. In this case, however, T_g values slightly higher than the curing temperature were obtained.

The three maleimide-ended HTPES polymers were also crosslinked at different temperatures, and the glass transition temperature was recorded as a function of the reaction time. Percentages of insoluble species were measured at the same time. All results are reported in *Figures 4* to *9*.

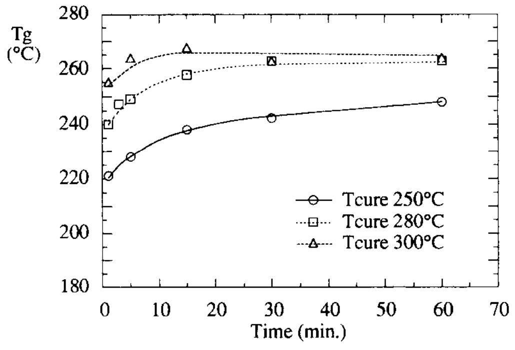

Figure 4 Glass transition temperatures of HTPES 1 as a function of curing time

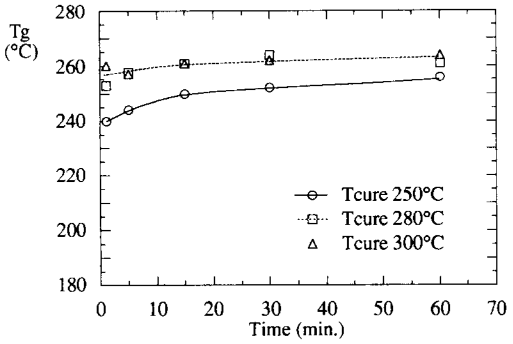

Figure 5 Glass transition temperatures of HTPES 2 as a function of curing time

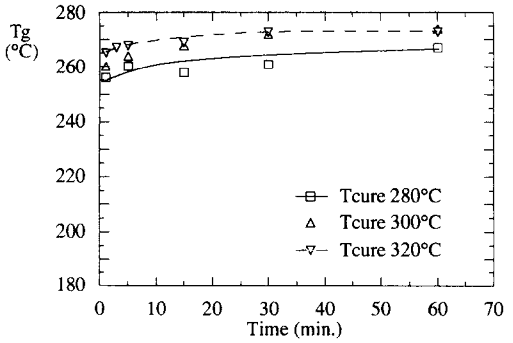

Figure 6 Glass transition temperatures of HTPES 3 as a function of curing time

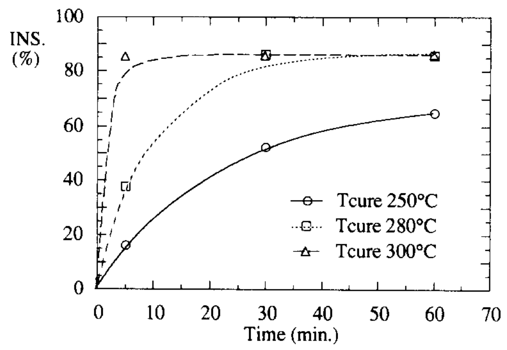

Figure 7 Percentage of insoluble species of HTPES 1 in cyclopentanone as a function of curing time

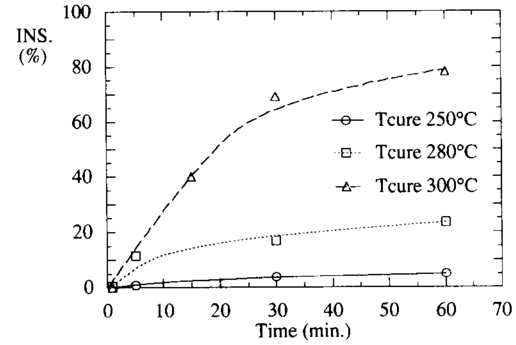

Figure 8 Percentage of insoluble species of HTPES 2 in cyclopentanone as a function of curing time

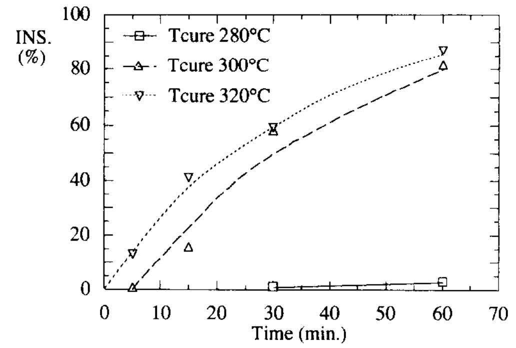

Figure 9 Percentage of insoluble species of HTPES 3 in cyclopentanone as a function of curing time

For all systems cured at 250°C, premature vitrification is occurring and T_g remains below the curing temperature. For low molecular mass polymers, the crosslinking reaction leads to a significant increase of molecular mass, with a corresponding increase in T_g. For higher molecular mass polymers, the starting T_g is already high and the increase of T_g due to crosslinking is not significant. In any case, the T_g values after crosslinking lie in the same range as those corresponding to linear high molecular mass homologues.

Insoluble fraction measurements are more sensitive to the degree of crosslinking. In *Figure 8*, for example, after 1 h of curing at different temperatures we observed large differences in the percentages of insoluble species. These differences are representative of different conversions for the crosslinking reaction. However, the corresponding T_g values, shown in *Figure 5*, are nearly the same. Similarly, Jin and Yee[14,15] have reported, for a maleimide-ended PES with a number-average molecular mass of 3000 g mol^{-1}, a nearly constant T_g after 70% conversion.

PES copolymers. Maleimide-ended PES copolymers were cured at 260°C and the glass transition temperatures were recorded as a function of the reaction time. Results are reported in *Figure 10*. The average number of molecular masses reported correspond to the molecular masses of the amine-ended precursor polymers.

The results are comparable to those obtained for HTPES samples. The T_g values obtained by extrapolation

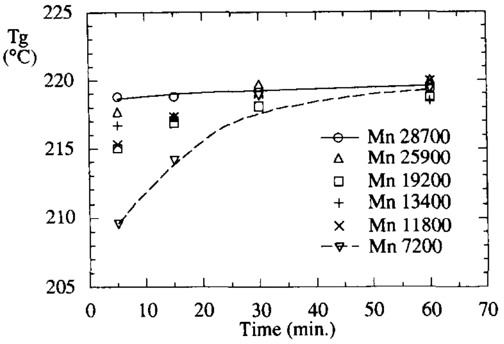

Figure 10 Glass transition temperatures of PES copolymer samples as a function of curing time at $T_{cure} = 260°C$

Table 3 T_g values obtained by extrapolation to infinite time of crosslinking reaction of PES copolymer samples

Sample	Extrapolated T_g (°C)
PES 1	219.2
PES 2	219.6
PES 3	218.4
PES 4	219.1
PES 5	219.7
PES 6	219.6

Table 4 T_g values before and after extraction of the soluble part and insoluble fraction for maleimide-ended PES copolymer samples crosslinked for 16 h at 260°C

Sample	T_g (°C)	T_g of insoluble part (°C)	Insoluble fraction (%)
PES	219	219	97
PES	218	218	97
PES	220	220	93
PES	221	219	93
PES	220	220	95
PES	220	220	96

to infinite time of reaction (T_g *versus* the reciprocal of time) are reported in *Table 3*. They are all in the same range and just below the infinite T_g calculated for the corresponding linear polymer.

Maleimide-ended PES copolymers were also cured for 16 h at 260°C in order to achieve complete crosslinking. Glass transition temperatures after crosslinking are reported in *Table 4* with their corresponding insoluble fractions. The T_g values of the samples after extraction of the soluble part are also reported in *Table 4*.

The T_g values in *Table 4* are in good agreement with those obtained from extrapolation to infinite time of crosslinking reaction. In *Figure 11*, the T_g values of polymers before and after crosslinking are reported as a function of number-average molecular masses before crosslinking. T_g values found in the literature[15] for low molecular mass bismaleimide(ether sulfone)s after crosslinking are also reported in *Figure 11*.

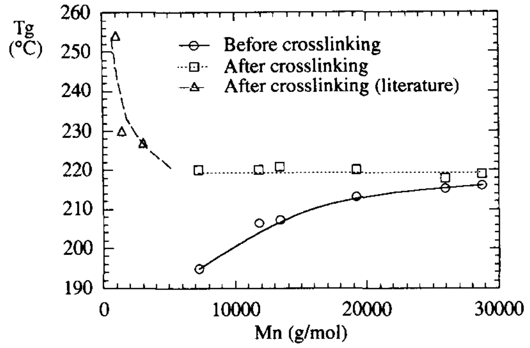

Figure 11 Glass transition temperatures of PES copolymer samples before and after complete crosslinking. Glass transition temperatures found in the literature for crosslinked low molecular mass bismaleimide(ether sulfone)s are also reported

For the studied polymers, the T_g values after crosslinking are not dependent on the precursor number-average molecular mass. They are in the same range as those of their non-reactive high molecular mass homologues. However, for lower molecular masses, substantial increases in T_g are observed[15]. Similar studies have been performed by Rietsch *et al.* for crosslinked polystyrene[16]. They reported significant linear increases in T_g with decrease of the number-average molecular mass prior to crosslinking, when the functionality of the junctions was greater than three. This effect of functionality on the T_g of crosslinked systems was explained by higher orientation of the chain segments near the crosslink nodules when the functionality was increased. In our case, the mean number of chain-ends reacting together to form a junction has been determined in a model compound study and is around three[17].

CONCLUSIONS

The molecular mass between entanglements for poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene) has been reported in the literature[18] and is equal to 2500 g mol^{-1}. Important increases in T_g values were observed above this number-average molecular mass. Contrary to what was mentioned in the Introduction, the independence of T_g with molecular mass when rubbery behaviour is observed is not then valid. The only available parameter influencing T_g when the molecular mass increases is the number of chain-ends. These chain-ends have a lower T_g by comparison with the entangled part of the chain. This lower T_g may be related to a higher free volume content or to higher configurational entropy of chain-ends. The resulting T_g of the polymer may be considered as a single phase mixture of a polymer fraction of infinite T_g and of chain-ends with a lower T_g.

In the range of molecular masses studied, T_g values after crosslinking are predominantly dependent on the intrinsic nature of the polymer and are not dependent on the final crosslink density. T_g values of partially crosslinked polymers are, however, related to the conversion level for a given polymer. The increase of T_g as a function of crosslinking time is directly linked to the decrease of chain-end content. However, this does not mean that this is a good way to determine the conversion level. Indeed, when the precursor molecular mass is already high, changes in T_g due to crosslinking are very small. In this case, determination of T_g is not a good way to follow the crosslinking reaction. The determination of the insoluble fraction is more sensitive to the conversion level.

These remarks are not valid if the molecular mass of the precursor polymer is very low. In this case, following the literature, important increases of T_g are observed and final T_g values are dependent on the crosslink density. For these systems, the low molecular mass between crosslinks restricts segmental mobility, hence the glass transition temperature increases. Moreover, for these low molecular mass species, the chemical nature becomes increasingly different from that of a high molecular mass polymer.

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REFERENCES

1 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21,** 569
2 Gibbs, J. H. and Di Marzio, E. A. *J. Chem. Phys.* 1958, **28,** 373
3 DiBenedetto, A. T. *J. Polym. Sci. Phys.* 1987, **25,** 1949
4 Mark, H. F. and Gaylord, N. G. (Eds) 'Encyclopedia of Polymer Science and Technology', John Wiley, New York, 1968, Vol. 8, p. 453
5 Van Krevelen, D. W. 'Properties of Polymers', 3rd edn, Elsevier Science, Amsterdam, 1990, p. 147
6 Fox, T. G. and Loshaek, S. *J. Polym. Sci.* 1955, **15,** 371
7 Di Marzio, E. A. *J. Res.* 1964, **68A,** 611
8 Nielsen, L. E. *J. Macromol. Sci. Rev. Macromol. Chem.* 1969, **C3**(1), 69
9 Maes, C., Devaux, J., Legras, R., Parsons, I. W. and McGrail, P. T. *J. Polym. Sci.: Part A: Polym. Chem.* 1994, **32,** 3171
10 Charlier, Y., Godard, P., Daoust, D. and Strazielle, C. *Macromolecules* 1994, **27,** 3604
11 Lyle, G. D., Senger, J. S., Chen, D. H., Kilic, S., Wu, S. D., Mohanty, D. K. and McGrath, J. E. *Polymer* 1989, **30,** 978
12 Garcia, D. *J. Polym. Sci.: Part B: Polym. Phys.* 1987, **25,** 1581
13 Takeda, S., Akiyama, H. and Kakiuchi, H. *J. Appl. Polym. Sci.* 1988, **35,** 1341
14 Jin, S. and Yee, A. F. *J. Appl. Polym. Sci.* 1991, **43,** 1849
15 Jin, S. and Yee, A. F. *J. Appl. Polym. Sci.* 1991, **43,** 1865
16 Rietsch, F., Daveloose, D. and Froelich, D. *Polymer* 1991, **17,** 859
17 Maes, C., Devaux, J., Legras, R. and Parsons, I. W. *J. Polym. Sci.: Part A: Polym. Chem.* in press
18 Herrmann-Schönherr, O., Schneller, A., Seifert, A. M., Soliman, M. and Wendorff, J. H. *Makromol. Chem.* 1992, **193,** 1955