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S0032-3861(96)00309-6

Polymer Vol. 37 No. 21, pp. 4841–4847, 1996
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0032-3861/96/$15.00 + 0.00

Synthesis, characterization and mechanical properties of networks prepared from poly(propylene glycol) di(ethylmaleate) and a trifunctional thiol

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(Received 7 December 1995; revised 14 February 1996)

One option to understand and possibly improve the properties of thermosets is to investigate well-defined polymer networks. Various novel, α, ω-ethylmaleate functionalized poly(propylene glycol)s were endlinked with a trifunctional thiol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol tris(3-mercaptopropionate) (EHPT). Model reactions of EHPT and diethyl maleate indicated that a substitution effect in the thiol is absent. Characterization of the model networks revealed that the molecular weight between junction points, M_c, calculated from the sol fraction (branching theory) agrees with the M_c calculated from the tensile storage rubber modulus E'. The glass transition temperature (T_g) decreases linearly with increasing M_c. The K_{Ic} (critical stress intensity factor) seems to be independent of the crosslink density. Copyright © 1996 Elsevier Science Ltd.

(Keywords: model networks; crosslink density; toughness)

INTRODUCTION

The mechanical properties of thermosets, in particular fracture toughness, are frequently discussed in terms of crosslink density. It has been proposed that the critical strain energy release rate G_{Ic} and the critical stress intensity factor K_{Ic} vary linearly with the molecular weight between the crosslinks M_c^1.

Recently, one of us published a paper on the properties of networks made from pure tris(4-isocyanatophenyl)thiophosphate (Desmodur RFE) and monodisperse poly(propylene glycol)s (PPG)[2]. The networks were proven to be well-defined. The general outcome of mechanical testing in the glassy state was that the materials are considerably tougher than various epoxies described in the literature[1,3]. A linear dependence was observed for K_{Ic} and M_c, although it is not clear whether this relationship addresses a network property or the chemical composition of the material. For, in this particular case as for other endlinked networks, increasing M_c brings along a larger amount of flexible material (PPG). Later, it was proven that the chemical composition determines K_{Ic}[4]. It would be interesting to evaluate networks, which are in the glassy state at room temperature. Polystyrene diols were thought to be likely candidates. However, on the basis of preliminary experiments it became clear that curing should be carried out at temperatures far above 100°C to ensure a proper melt flow. In this region the simple addition of isocyanate and hydroxyl groups to give urethane bonds can be obscured by side-reactions such as the formation of allophanates and isocyanurates. These considerations prompted us to develop a model system with a wider processing window.

An extensive literature search for simple addition reactions resulted in the selection of the Michael addition of thiols to electron-deficient olefins. Chain extension of bismaleimides and bismaleates by bisthiols has also been described in the literature[5–7]. As a first step it was proposed to develop a model system consisting of a PPG with ethylmaleate endgroups and a commercially available trifunctional thiol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol tris(3-mercaptopropionate) (EHPT). Quite recently, a similar system was described in the literature based on diallyl-poly(tetrahydrofuran) and a tetrafunctional thiol (radical-mediated addition)[8]. However, no attention was paid to the mechanical properties of these materials in the glassy state.

This paper describes the chemistry and characterization of a model system, based on EHPT and various modified PPG's. A detailed comparison of the experimental results with those of the PPG-trisisocyanate system will be published elsewhere.

EXPERIMENTAL

Materials and methods

Poly(propylene glycol)s PPG(425), PPG(725), PPG(2000) (Aldrich), sodium acetate (NaOAc) (Merck), maleic anhydride (MA) (Baker), tetrahydrofuran (THF) (Baker), silica gel (Janssen), aluminium oxide (Janssen), magnesium sulfate (Janssen), dicyclohexylcarbodiimide (DCC) (Janssen), ethanol (Riedel-de Haen), dichloromethane (Merck), copper(I)

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chloride (CuCl) (Janssen), diazabicyclooctane (DABCO) (Janssen), chloroform-d_1 ($CDCl_3$) (Merck), acetic anhydride (Ac_2O) (Merck), diethyl ether (Merck), hydrochloric acid 37% (Merck), n-hexane (Riedel-de Haen), methyl-3-mercaptopropionate (MMP) (Aldrich), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol tris(3-mercaptopropionate) (EHPT) (Aldrich) and di(ethyl maleate) (Aldrich) were used as received.

The ^1H n.m.r. spectra were recorded with a Bruker ACF200 (200 MHz) spectrometer under standard conditions. G.p.c. experiments were conducted with equipment consisting of a Rheodyne injector, a Gilson 302 pump, a Waters 410 refractometer, a Severn Analytical SA 6503 detector and Styragel columns 100, 500, 1000 and 10 000 Å using THF as the eluting agent. Calibration was carried out with polystyrene samples. H.p.l.c. experiments were conducted with equipment consisting of a HP 1090 system, a Linear UV VIS 203 spectrometer, a Nucleosil 120-5C18 column and a HP 1000 labdata system using acetonitrile/water mixtures as the eluting agents. Dynamic mechanical measurements in tension were performed with a Rheometrics RSA-2 Solids Analyzer at a frequency of 1 Hz. The density of each sample was measured with a helium pycnometer. K_{Ic} test bars were prepared from 6 mm thick sheets. Specimen dimensions were approximately $6 \times 8 \times 36\,mm^3$. Samples were prenotched with a single point fly cutter (notch tip radius of 0.1 mm) and notched by sliding a razor blade into the prenotch. The quasi static K_{Ic} measurements were performed in single edge notched bend geometry according to the protocol for K_{Ic}/G_{Ic} testing prepared by ESIS[9]. The tests were performed on a Zwick 1474 tensile tester, testing speed $10\,mm\,min^{-1}$, at 100°C below the glass transition temperature (T_g).

Preparation of PPG di(ethylmaleate)

All compounds were made in the same way. The following procedure serves as an example.

A mixture of 201.3 g (0.28 mol) PPG(725), 81.6 g (0.83 mol) MA, 4.5 g (0.05 mol) NaOAc and 400 ml THF was stirred at reflux conditions for 24 h. The reaction mixture was then cooled to room temperature and filtered to remove any undissolved NaOAc. The solvent THF was removed *in vacuo* using a rotavap. Extraction of a diethyl ether solution (600 ml) of the remainder with six portions of 250 ml of demineralized water, drying on magnesium sulfate, a final filtration over aluminium oxide and evaporation of the solvent gave 251.3 g (0.27 mol, yield: 96%) of a colourless oil, PPG(725) dimaleate, according to ^1H n.m.r. spectrometry.

A mixture of 167.6 g (0.81 mol) DCC, 0.86 g (0.008 mol) CuCl and 200 ml ethanol (dried on mol. sieves 3 Å) was stirred at reflux conditions for 3 h and subsequently cooled to room temperature. After filtration of the reaction mixture and evaporation of the solvent, the oily remainder was dissolved in 400 ml of n-hexane and stirred with aluminium oxide to remove the catalyst CuCl. A final filtration step over aluminium oxide and evaporation of the solvent gave 182.0 g (0.72 mol, yield 89%) of a colourless oil, the ethanol adduct of DCC (DCC·EtOH), according to ^1H n.m.r. spectrometry.

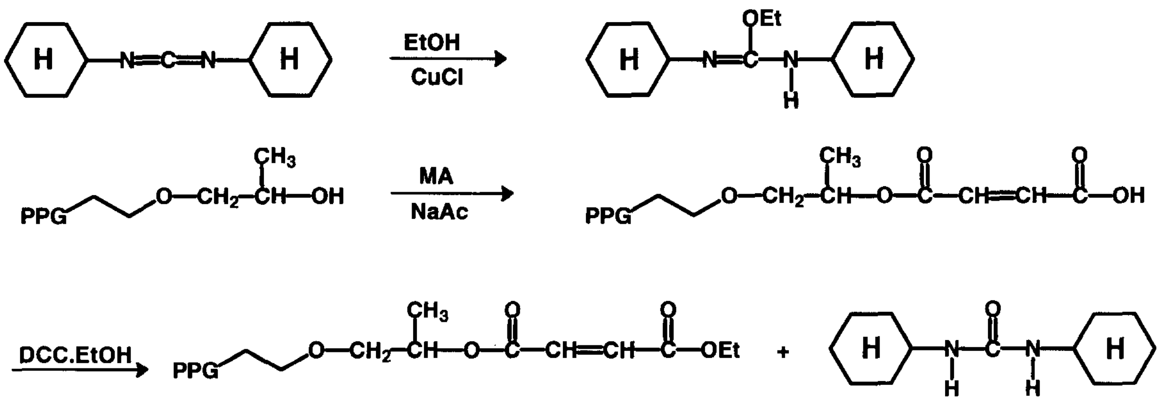
A solution of 182.0 g (0.72 mol) DCC·EtOH in 200 ml dichloromethane was added dropwise, while stirring, to an ice-cooled solution of 251.3 g (0.27 mol) PPG(725) dimaleate in 400 ml dichloromethane. After evaporation of the solvent, the viscous remainder was heated at 80°C for 2 h. During heating a white solid precipitated. The cooled reaction mixture was stirred with 500 ml diethyl ether, filtered to remove the dicyclohexyl ureum and subsequently stirred with 300 ml of 10% hydrochloric acid to destroy the excess of DCC·EtOH. The organic layer was washed with 300 ml water, dried on magnesium sulfate, filtered over aluminium oxide and finally evaporated to give 185.6 g (0.18 mol, yield: 64%) of a colourless oil, PPG(725) di(ethylmaleate).

Preparation of PPG(725) diacetate

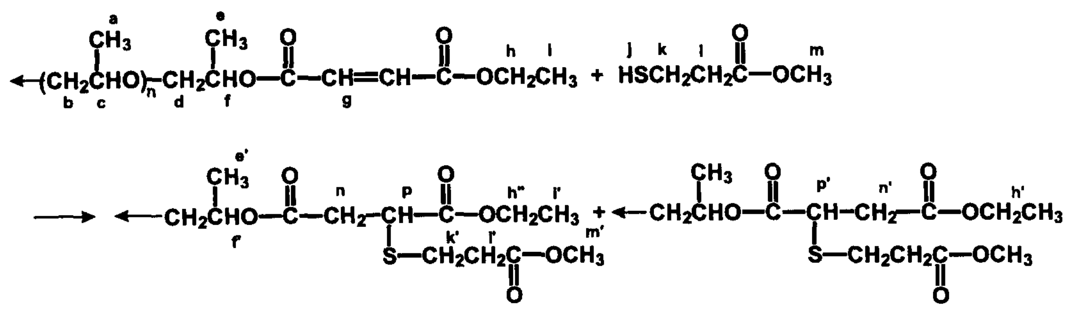
A mixture of 50.0 g (0.07 mol) of PPG(725), 28.1 g (0.28 mol) of Ac_2O, 1.13 g (0.014 mol) of NaOAc and 200 ml of THF was stirred at reflux conditions for 24 h. The reaction mixture was then cooled to room temperature and filtered to remove any undissolved NaOAc. The solvent THF was removed *in vacuo* using a rotavap. Extraction of a diethyl ether solution (300 ml) of the remainder with six portions of 150 ml of demineralized water, drying on magnesium sulfate, a final filtration over aluminium oxide and evaporation of the solvent gave 45.0 g (0.05 mol, yield: 71%) of a colourless oil, PPG(725) diacetate, according to ^1H n.m.r. spectrometry.

Preparation of rubber sheets

All rubber sheets were prepared in the same way. The following procedure serves as an example.



Scheme 1



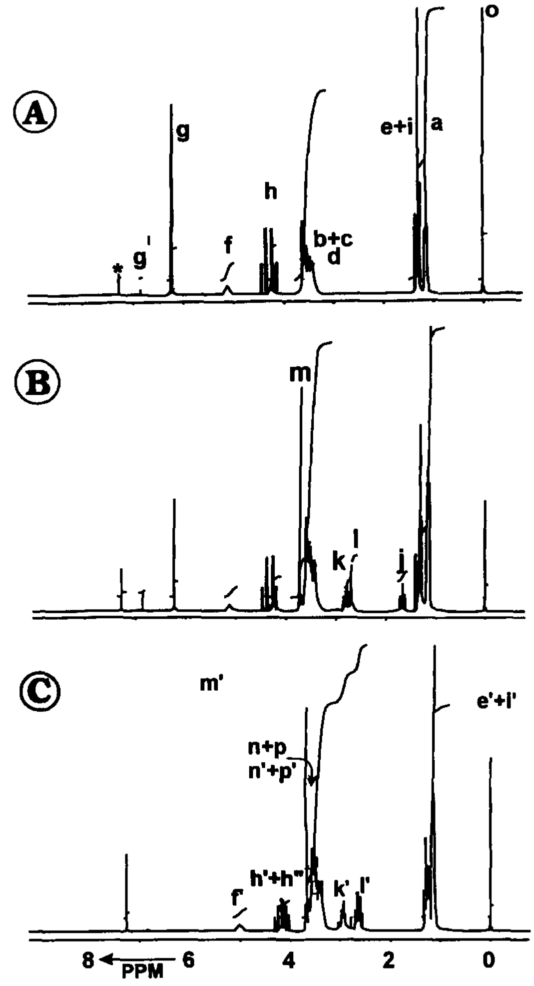


Figure 1 ^{1}H n.m.r. spectra of: (A) PPG(725)diEM and the reaction mixtures of PPG(725)diEM and MMP (1 mol% of DABCO) after (B) 5 min and (C) 17 h at 22°C (* = $CDCl_3$, ○ = TMS)

After degassing 3.09 g (7.7 mmol) EHPT by three vacuum-nitrogen cycles to remove traces of oxygen, 0.026 g (0.2 mmol) DABCO was added. The mixture was stirred under gentle heating to dissolve the DABCO crystals, after which the reaction mixture was cooled to room temperature. In a subsequent step, 11.7 g (11.6 mmol) PPG(725) di(ethylmaleate) was added, followed by a degassing procedure. The mixture was rapidly stirred for 30 min at room temperature and finally poured into a mould. Curing at room temperature (17 h), 60°C (8 h) and 100°C (17 h) gave a slightly yellow, flexible sheet.

RESULTS AND DISCUSSION

Chemistry of network formation

The synthetic route to PPG's with ethylmaleate endgroups is outlined in *Scheme 1*. PPG's and their derivatives cannot be easily purified by crystallization or distillation, which prompted us to develop a route with 100% chemoselectivity, while reactions are directed towards 100% conversion by using an excess of the appropriate reagents. In addition, it should be possible to remove the excess of chemicals by simple procedures like extraction or filtration. All details are described in the Experimental section.

Reaction of a particular PPG with maleic anhydride and the catalyst sodium acetate in THF at reflux conditions gave the carboxylic acid endcapped analogue. In a subsequent step the reaction product was esterified in the presence of the ethanol adduct of DCC based on procedures described in the literature[10].

Table 1 Molecular weights of PPG and PPGdiEM obtained from ^{1}H n.m.r. spectrometry and g.p.c.

PPG			
	M_n(^{1}H n.m.r.)^a	M_n(g.p.c.)	M_w/M_n(g.p.c.)
425	430	590	1.11
725	740	1030	1.15
2000	2040	2320	1.35
PPGdiEM			
M_n(theor)	M_n(^{1}H n.m.r.)^a	M_n(g.p.c.)	M_w/M_n(g.p.c.)
690	660	830	1.14
990	1010	1170	1.22
2290	2500	2460	1.34

^{a} Assuming an average functionality of 2.0

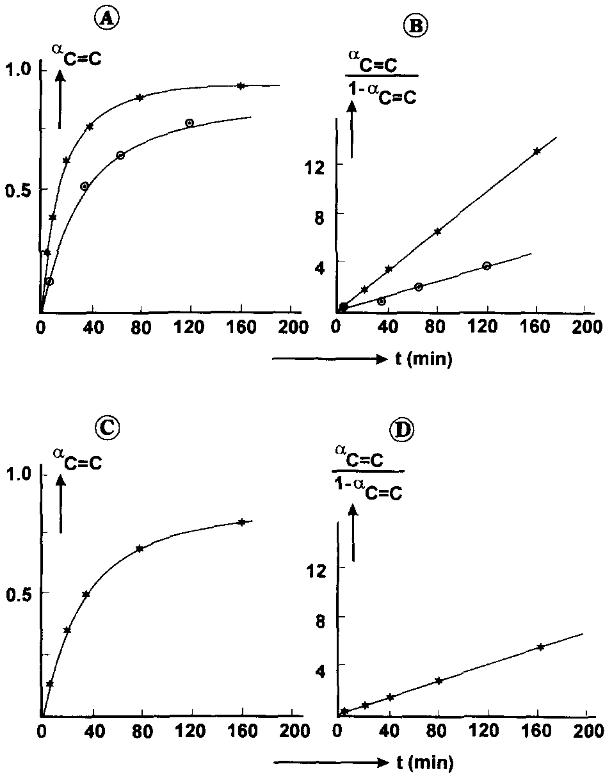


Figure 2 Reaction of: (A, B) PPG(725)diEM with MMP (1 mol% of DABCO) at 22°C (O) and 58°C (*) and (C, D) EHPT with DEM (1 mol% of DABCO) in PPG(725)diAc at 22°C

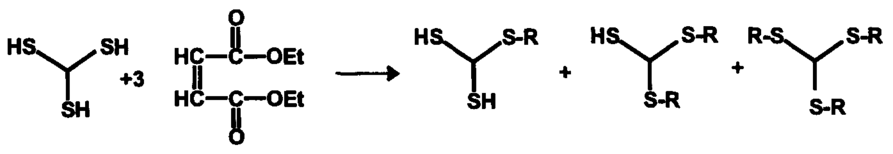
A typical ^{1}H n.m.r. spectrum of PPG(725) di(ethylmaleate), PPG(725)diEM, together with all peak assignments, is shown in *Figure 1A*. The singlet at 6.2 ppm due to H(g) indicates that the majority of endgroups are still *cis* configurated (maleate). According to the small peak at 6.85 ppm due to H(g′), isomerization to the *trans* configuration (fumarate) does occur, although to a minor extent (less than 5%). The molecular weights of the PPG's and the modified PPG's obtained from ^{1}H n.m.r. and g.p.c. measurements are compiled in *Table 1*. In all cases the ratio of CH(f) to CH(g + g′) amounts to 2.0, which means that no unsaturation disappears during the experiment. M_n can then be calculated from the ^{1}H n.m.r. spectrum assuming that the average functionality amounts to 2.0. In the case of the parent PPG's a good agreement exists between the values given by the manufacturer and those calculated from the ^{1}H n.m.r. spectra. The same holds when comparing the theoretical and calculated values of PPGdiEM. The M_n values from g.p.c. measurements are, in general, considerably higher than those obtained by ^{1}H n.m.r. spectrometry, probably due to the calibration procedure (polystyrene samples). Henceforth, the M_n values obtained by ^{1}H n.m.r. spectrometry will be used to calculate the proper amount of crosslinker when preparing model networks.

The next part considers the chemistry that takes place during network formation. The Michael addition of thiols to electron-deficient olefins can be catalysed by bases[11]. Curing of mixtures of PPGdiEM and EHPT in the presence of tri-n-butylamine, diazabicyclooctane (DABCO) or tetramethylguanidine, i.e. with increasing base strength, learned that DABCO offers an optimal balance between processability and reactivity. Several model experiments were carried out, viz. the reactions of methyl-3-mercaptopropionate (MMP) with PPG(725) diEM at various temperatures and the reaction of the crosslinker EHPT with diethyl maleate (DEM) in the presence of PPG(725) diacetate, PPG(725)diAc, as a diluent.

The reaction of PPG(725)diEM with two equivalents of MMP and 1 mol% of DABCO relative to the amount of thiol groups was followed by means of ^{1}H n.m.r. spectrometry. *Figure 1* displays the spectra of the reaction mixtures after 5 min (13% conversion) (*B*) and 17 h (100% conversion) (*C*) at 22°C. Upon addition of the thiol to the unsaturation the spectral features change according to ones expectation. The triplet due to SH(j) and the singlets due to H(g) and H(g′) disappear completely, while several peaks due to H atoms of the endgroups show a considerable shift. The addition product exists in two isomeric forms (*Figure 1*). The symmetrical shape of the multiplet at 4.2 ppm due to H(h′ + h″) of the OCH_2CH_3 endgroup suggests that the isomers are present in equal amounts.

The kinetic behaviour of the model system at 22 and 58°C is shown in *Figures 2A* and *B*. The conversion of unsaturations proceeds according to a second order process as concluded from the linearity of a plot of $\alpha(C=C)/1-\alpha(C=C)$ vs time. According to the ^{1}H n.m.r. spectra no side-reactions occur, which holds even up to a reaction temperature of 180°C (2 h).

The process of network formation can be influenced by substitution effects, i.e. the reactivity of a particular SH group depends on the reaction state of the other arms of EHPT[12]. Therefore, EHPT was reacted with three equivalents of DEM (1 mol% of DABCO) dissolved in PPG(725)diAc in order to simulate the actual crosslinking system. The overall kinetics of the model reaction at 22°C (*Figures 2C* and *D*) closely resemble that of the reaction between PPG(725)diEM and MMP at 22°C (*Figures 2A* and *B*), inasmuch as the rate constants are equal. During the experiment samples were withdrawn for analysis by means of h.p.l.c. *Figure 3* shows the h.p.l.c. diagrams of the reaction mixtures obtained after 0, 25, 60 and 1080 min at 22°C. Compounds **1** and **2** are EHPT and DEM, respectively. Compound **2*** appeared to be diethyl fumarate (DEF), which is most probably generated via isomerization of DEM (*Scheme 2*). For steric reasons one would expect DEF to be less reactive than DEM towards nucleophilic attack by the thiol.



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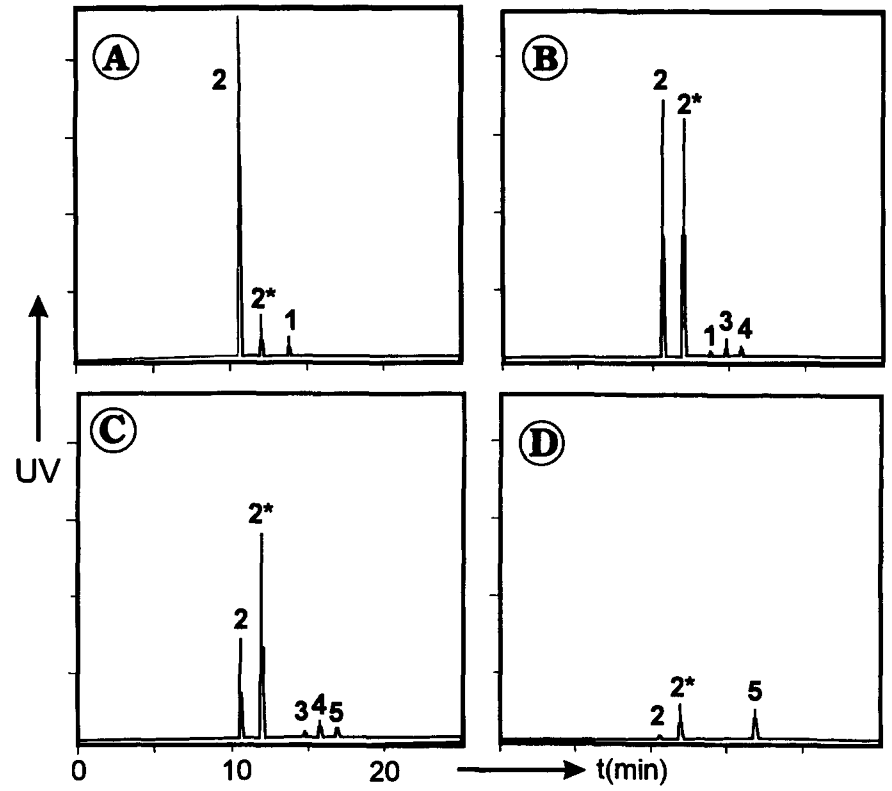
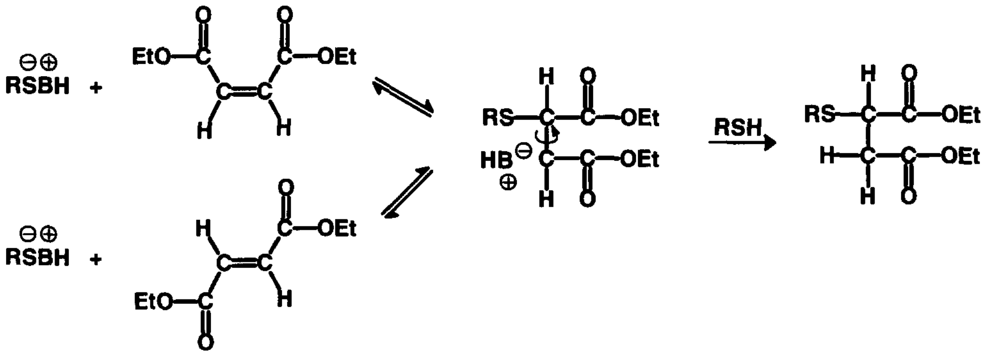


Figure 3 H.p.l.c. diagrams of the reaction mixtures from EHPT and three equivalents of DEM in PPG(725)diAc (1 mol% of DABCO) at 22°C after 0 (A), 25 (B), 60 (C) and 1080 min (D) (2* = DEF)



Scheme 2

However, $\alpha(C{=}C)/1-\alpha(C{=}C)$ vs time (*Figure 2D*) gives a single straight line, indicating that the rate constant k does not change during the reaction.

These observations are in line with literature on the addition of various thiols to diallyl maleate (DAM) and diallyl fumarate (DAF), catalysed by tertiary amines[13]. The main conclusions are, firstly, that isomerization precedes the formation of succinate products; no isomerization of DAM occurs in the presence of the base only. Secondly, that upon increasing acidity of the thiol the difference in reactivity between DAM and DAF seems to disappear. In the case of EHPT, hydrogen bonding between SH and the ester linkage (see also *Figure 1*) enhances the acidity of the thiol and can, therefore, be responsible for the appearance of one rate constant.

Compounds **3**–**5** are the mono-, di- and trisubstituted derivatives of EHPT, which were identified by means of mass spectrometry. *Figure 4* describes the fate of all compounds, including the starting compound **1**, as a function of the overall conversion of SH groups. The experimental data all coincide with the theoretical lines as calculated for random reactivity (Bernoulli distribution). The outcome of this experiment indicates that substitution effects are most probably absent.

Network formation and characterization

Mixing of a particular PPGdiEM and EHPT, molar ratio (C=C):SH = 1:1, in the presence of 1 mol% of DABCO resulted in a clear homogeneous liquid. Curing in a mould at room temperature (17 h), 60°C (8 h) and 100°C (17 h) afforded a colourless or slightly yellow, flexible sheet. The mechanical properties of the three rubber sheets as well as the the results from sol-gel analysis and dynamic mechanical analysis (d.m.a.) are listed in *Table 2*.

The sol fractions vary between 1.3 and 2.2% and increase with increasing molecular weight of the PPGdiEM. In general, off-stoichiometry and decreased mobility at the end of the polymerization result in incomplete conversion of reactive groups. It is also possible that a SH group of a particular molecule, large or small, reacts with an unsaturation already connected to this molecule (cyclization). In all cases the cured material contains a soluble fraction, that can be extracted by a good solvent. The presence of a sol fraction implicates a decreased concentration of elastically active crosslink points as compared to the ideal case, leading to a decreased rubber modulus. Definite proof for either of these explanations should be obtained by determination of the residual amounts of thiol and fumarate (maleate) groups, which is, however, difficult from an analytical point of view. Sol fractions of 1–2% have also been reported for diallylpoly(tetrahydrofuran)-tetrathiol rubber networks[8].

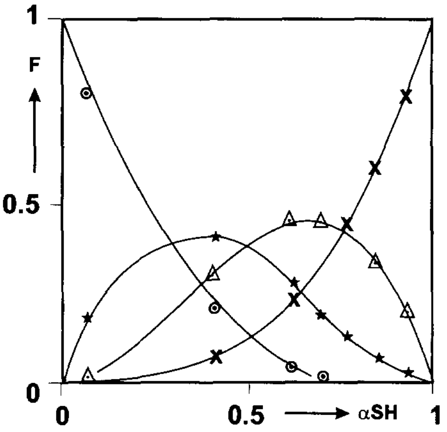


Figure 4 Reaction of EHPT with DEM in PPG(725)diAc (1 mol% of DABCO) at 22°C; fractions of EHPT (○) and the monosubstituted (∗), disubstituted (△) and trisubstituted (x) derivatives of EHPT vs total conversion of SH groups

From the tensile storage rubber modulus E' one can calculate the molecular weight between the crosslinks M_c, according to the formula $E'/3 = A\rho RT/M_c$ (A = front factor, ρ = density, R = gas constant, T = temperature)[14]. Two extreme cases have been treated, viz. $A = 1$ (affine limit) and $A = 1/3$ (phantom limit). By using the theory of branching processes W_{sol} is transformed into the conversion α of reactive groups and subsequently into M_c at that conversion[12]. A reasonable agreement exists between $M_c(\alpha)$ and $M_c(E')$ for A equal to 1. We expect the affine limit to be relevant since E' was measured at small strain and frequency using samples with little sol and no solvent.

Figure 5 shows a diagram of T_g vs $1/M_c(\alpha)$. A straight line emerges indicating that T_g is inversely proportional to M_c, in contrast to the previously examined PPG-trisisocyanate networks for which T_g was found to be inversely proportional to M_n(PPG) only[15]. The results presented here suggest that the chain mobility related to T_g, as measured by d.m.a., not only involves the PPG part, but also the succinate parts and the arms of EHPT. Extrapolation of T_g (network) towards very high M_c gives a value of −75°C, which corresponds well with the published T_g of high molecular weight PPG[16]. The second line represents the copolymer effect[17]. The data points are obtained by combining T_g of high molecular weight PPG and the T_g of the tris(diethylmaleate) derivative of EHPT (−42°C) multiplied by the weight fractions of each component. The difference between the two lines accounts for the effect of crosslinking and varies proportional to $1/M_c$.

Of significant interest to us are the mechanical properties of polymer networks in the glassy state, in particular the fracture toughness. Therefore, the critical stress intensity factor K_{Ic} was measured at 100°C below the T_g of a specific sample. The K_{Ic} values, listed in *Table 2*, are comparable to those obtained for PPG-trisisocyanate networks[3]. Interestingly, K_{Ic} is high and seems to be independent of crosslink density. Recently, it was shown that crosslink density does not significantly contribute to K_{Ic} of a polymer network in the glassy state. A study of PPG-trisisocyanate networks with designed defects revealed that K_{Ic} is proportional to the weight fraction

Table 2 Tensile storage rubber modulus (E'), density (ρ), sol fraction (w_s), glass transition temperature (T_g) and stress intensity factor (K_{Ic}) of networks from EHPT and PPG(425)diEM (**1**), PPG(725)diEM (**2**) and PPG(2000)diEM (**3**)

Compound	M_c(theor)	E'(MPa) (50°C)	ρ (kg m^{-3})	w_{sol}%	T_g (°C)	K_{Ic} (MPa m$^{0.5}$)
1	890	3.9 (0.2)	1170	1.3 (0.2)	−27 (0.5)	3.1 (0.3)
2	1240	4.0 (0.2)	1130	1.5 (0.2)	−40 (0.5)	4.2 (0.2)
3	2730	1.8 (0.1)	1060	2.2 (0.3)	−58 (0.5)	4.3 (0.3)

	α (w_{sol})	$M_c(E')$ ($A = 1$)	$M_c(E')$ ($A = 1/3$)	M_c (α)
1	0.92	2430	810	2080
2	0.92	2290	760	2620
3	0.90	4650	1550	5600

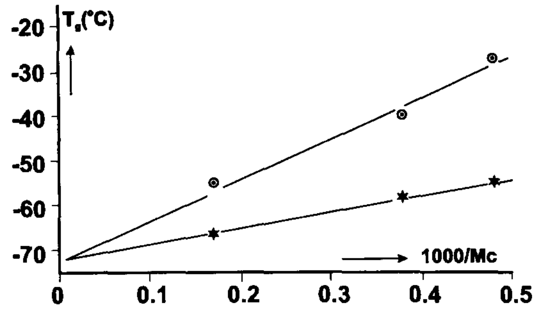


Figure 5 T_g (O) and the calculated copolymer T_g(*) vs $1/M_c(\alpha)$ for various PPGdiEM-EHPT networks

of polyether present[18]. Our findings are in accordance with the former observations. Assuming the arms of the crosslinker EHPT to be flexible too, it follows that the total fraction of flexible material remains constant. A detailed discussion of these phenomena will be presented elsewhere.

CONCLUSIONS

Prepolymers with ethylmaleate endgroups can be made by reaction of poly(propylene glycol)s with maleic anhydride and subsequent esterification in the presence of the ethanol adduct of dicyclohexylcarbodiimide. Crosslinking of these prepolymers with a trifunctional thiol, EHPT, proceeds via a base-catalysed Michael addition. A substitution effect appears to be absent as concluded from a model experiment with diethyl maleate and EHPT. The maleate endgroups partly isomerize to the fumarate analogues, while no change of the overall rate constant is observed. Reactions proceed to high conversion without detectable side-products, even up to a reaction temperature of 180°C.

Characterization of the model networks by sol-gel analysis and dynamic mechanical analysis reveals that a reasonable agreement exists between M_c calculated from the sol fraction (branching theory) and M_c calculated from the tensile rubber modulus E'. T_g decreases linearly with increasing M_c. The critical stress intensity factor K_{Ic} of these networks seems to be independent of the crosslink density and proportional to the fraction of flexible chains.

ACKNOWLEDGEMENT

The authors wish to thank Mr T. A. Verstappen (h.p.l.c.), Mr G. R. Struijk (mechanical testing) and Mr M. A. van Es (d.m.a.) for carrying out part of the experimental work.

REFERENCES

1 Pearson, R. D. and Yee, A. F. *J. Mater. Sci.* 1989, **24**, 2571
2 Levita, G. in 'Rubber-Toughened Plastics', Advanced Chemistry Series 222, Washington, 1989
3 Bos, H. L. and Nusselder, J. J. H. *Polymer* 1994, **35**, 2793
4 Fischer, M. *Adv. Polym. Sci.* 1992, **100**, 313
5 Dix, L. R., Ebdon, J. R. and Hodge, Ph. *Eur. Polym. J.* 1995, **31**, 653
6 Crivello, J. V. *J. Polym. Sci., Polym. Chem.* 1976, **14**, 159
7 White, J. E. and Scaia, M. D. *Polymer* 1984, **25**, 850
8 Jong, L. and Stein, R. S. *Macromolecules* 1991, **24**, 2323
9 Williams, J. G. and Cawood, M. J. *Polymer Testing* 1990, **9**, 15
10 Joos, B., Schmidts, B. and Funke, W. *Makromol. Chem.* 1987, **188**, 1375
11 March, J. 'Advanced Organic Chemistry', 3rd edn, Wiley, New York, 1985
12 Tiemersma-Thoone, G. P. J. M., Scholtens, B. J. R., Dusek, K. and Gordon, M. *J. Polym. Sci. Polym. Phys.* 1991, **29**, 463
13 Oswald, A. A. and Naegele, W. *J. Org. Chem.* 1966, **31**, 830
14 Mark, J. E. and Erman, B. 'Rubber-like Elasticity. A Molecular Primer', Wiley, New York, 1988
15 Steeman, P. A. M. and Nusselder, J. J. H. *Polymer Gels Networks* 1995, **3**, 159
16 Lee, W. A. and Rutherford, R. A. 'Polymer Handbook', Wiley, New York, 1975
17 Fox, T. G. *Proc. Am. Phys. Soc.* 1956, **1**, 123
18 Nusselder, J. J. H. and Bos, H. L. *Macromol. Chem. Macromol. Symp.* 1995, **93**, 17