Polyurethane networks based on poly(ethylene ether carbonate) diols

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Ethylene carbonate was bulk-polymerized via a ring-opening mechanism using monoethylene glycol (MEG) as initiator and sodium stannate trihydrate as heterogeneous catalyst. Due to the loss of CO_2 from a fraction of the repeat units during polymerization, a copolymer comprised of ethylene oxide and ethylene carbonate repeat units, poly(ethylene ether carbonate) (PEEC) resulted. The purified polymers were shown to be hydroxy-terminated by acetylation of the chain end and subsequent titration. Molecular weights higher than $\bar{M}_n \sim 4600$ g mol^{-1} were not attainable due to a prevailing level of MEG present adventitiously in the system. PEEC-based polyurethane networks resulted from the reaction of four different molecular weight PEEC diols with a trifunctional isocyanate, triphenylmethane triisocyanate. Network characterization included equilibrium swelling, determination of sol content by solvent extraction, glass transition (T_g) by differential scanning calorimetry, and tensile properties by stress–strain measurements. A network curing schedule of 7 days produced networks with high sol contents (10%). Extension of the curing schedule to 19 days produced networks with low sol contents (2–5%) with the minimum sol content centred about a stoichiometric ratio, OH/NCO, of approximately one. Tensile strength ranged from 1.3 to 12.3 MPa, modulus ranged from 1.5 to 26 MPa, and strain at break ranged from 60 to 240 for networks from PEECs of $\bar{M}_n$ in the range of 730–4400 g mol^{-1}. Tensile properties, T_gs and equilibrium swelling measurements indicated that at increased isocyanate content the crosslink density of the network increased, possibly due to side reactions such as isocyanurate or allophanate formation.

(Keywords: polyurethane networks; poly(ethylene ether carbonate); polymerization)

INTRODUCTION

Copolymers of cyclic ethers and CO_2, i.e. polycarbonates, are of interest as soft segment diol prepolymers for polyurethane thermoplastic and network polymers. They are of particular interest as potential solid rocket propellant binders, and compared to the commonly used hydrocarbon polymeric binders such as hydroxy-terminated polybutadiene, simple aliphatic polycarbonates possess a high O_2 content and incorporate CO_2 as an inexpensive building block. High O_2 content usually results in a polymer having a low heat of combustion (ΔH_{comb}). For example, an alternating copolymer of CO_2 and ethylene oxide (EO) has a $\Delta H_{comb} = 3320$ kcal mol^{-1}, about one-third that of polyethylene[1]. Hydroxyl functionality enables facile network-forming reactions with multifunctional isocyanates.

There are generally two modes of aliphatic polycarbonate formation, either by direct copolymerization of cyclic ethers with CO_2 (**1**) or ring-opening polymerization of cyclic carbonates (**3**) (*Scheme 1*). Inoue *et al.*[2,3] first reported the synthesis of high molecular weight polypropylene carbonate by the alternating copolymerization of propylene oxide (R = CH_3) and CO_2. Since then the copolymerization of cyclic ethers and CO_2 has been reported quite extensively. The discovery of *immortal* polymerization enabled the synthesis of well defined polymers from the alternating copolymerization of CO_2 and oxiranes[5].

The reaction of cyclic ethers with CO_2 can also be used to form cyclic carbonates[6] (**2**). Thus an alternative approach to copolymerization is the ring-opening polymerization (**3**) of the intermediate cyclic carbonate which contains the desired polycarbonate backbone structure. The ring-opening polymerizations of propylene carbonate (**3**, R = CH_2) and ethylene carbonate (EC) (**3**, R = H) have been shown to result in a loss of CO_2 during the course of the reaction to produce copolymers comprised of propylene oxide and propylene carbonate repeat units[7], and EO and EC repeat units, respectively[8–26]. Vogdanis and Heitz employed a variety of catalysts for the polymerization of EC, ranging from dibutyltin dimethoxide to butyllithium, and found that the retention of CO_2 decreased as the alkalinity of the catalyst increased[22]. Under optimum conditions the maximum retention of CO_2 in the copolymer was 50 mol%, producing an alternating copolymer of EO and EC, i.e. poly(ethylene ether carbonate) (PEEC).

Harris has reported the use of inorganic salts such as sodium stannate trihydrate (SS) as heterogeneous catalysts in EC polymerization[23–25]. The authors utilized a diol initiator to limit molecular weight, and they reported the products to be low molecular weight copolymers of EO and EC. Harris and McDonald found

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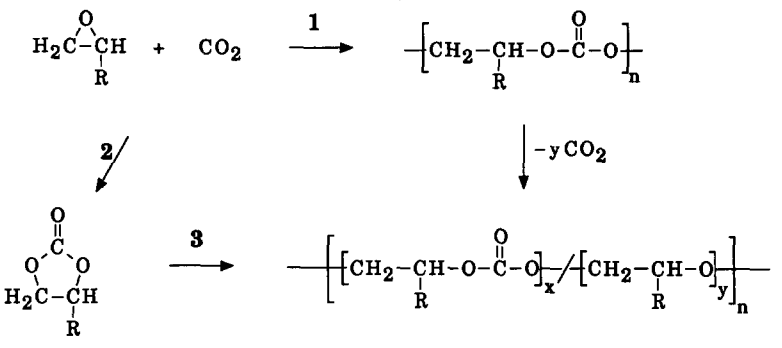
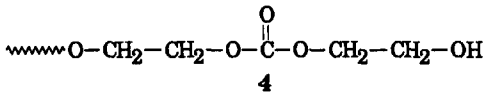


Scheme 1

that both 2-hydroxyethyl carbonate (**4**) and 2-hydroxyethyl ether (**5**) end groups are present initially in the polymerization mixture; however, only **5** is present during the latter stages of polymerization[25].



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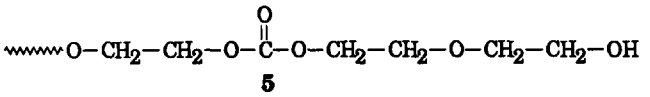

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We investigated the synthesis of PEEC using the organotin catalysts dibutyltin diacetate, dibutyltin dilaurate and dibutyltin dimethoxide, and the inorganic catalyst, SS, and offered a mechanism for polymerization which explains the loss of CO_2 from at least every other repeat unit[27]. SS was successfully utilized to synthesize a series of PEEC copolymers of varying molecular weights, high EC incorporation (>40 mol%) and terminal hydroxyl functionality. A description of PEEC oligomer synthesis and characterization and subsequent PEEC-based network formation and characterization are presented in this paper.

EXPERIMENTAL

Materials

EC (99.5%, Texaco Chemical Co.) was distilled from calcium hydride under vacuum prior to use. Monoethylene glycol (MEG, anhydrous, 99 + %, Aldrich Chemical Co.), 1,2-dichloroethane (anhydrous, Aldrich Chemical Co.) and SS (Alfa Chemical Co.) were used as received. Methylene chloride (J. T. Baker) was distilled from calcium hydride prior to use.

Triphenylmethane triisocyanate (TTI) (20 wt% methylene chloride solution, Mobay Corp.) initially was used as received. Assay of the isocyanate content of this solution was performed by reacting the isocyanate groups with excess n-butylamine (99%, Aldrich Chemical Co.) followed by titration with acid (0.1 M HCl) (ASTM 1683-74). The measured concentration of TTI was found to be 21.2 wt%. In later investigations, TTI was purified by a vacuum distillation procedure which has been described elsewhere[28].

Procedures

Synthesis of PEEC. The procedure for PEEC oligomer synthesis, using SS catalyst, has been described in detail elsewhere[27]. The oligomers were dried *in vacuo* at 80°C for at least 7 days prior to hydroxyl functionality determination and subsequent network formation.

Hydroxyl functionality determination. The hydroxyl functionality of the PEEC oligomers was measured using an acetylation procedure developed by Dee *et al.*[29]. The procedure was essentially the same as that reported by us for other hydroxy-terminated prepolymers[28].

Network formation. The network forming procedure was as follows: a sample of PEEC (3–4 g) was weighed accurately into a 2 oz bottle, and an appropriate amount of 1,2-dichloroethane was added to attain a 50 wt% solution. Following dissolution, the desired quantity of TTI solution was added along with a methylene chloride solution of dibutyltin dilaurate (0.01 wt% catalyst based on total solids weight). The solution was mixed and then transferred to a baked-out (30 min at 150°C) aluminium weighing pan. The pan was placed in a 40°C vacuum oven and a gentle vacuum applied (10–15 mm in Hg). This gentle removal of the solvents (quantitatively removed in 2–3 h) produced clear films, free of voids, which were cured further at 40°C for 3 days total, followed by 2 days at 60°C and finally either 2 or 14 days at 80°C. The films were slowly cooled to room temperature overnight to allow relaxation of residual stresses, after which time they were removed from the pans.

Extraction and swelling studies. Extraction and swelling studies were carried out using anhydrous 1,2-dichloroethane according to our published procedure[28].

Tensile properties. Tensile testing was performed on microdumb-bell samples (4 × 0.5 × 0.1 cm) stamped from solvent-extracted films, using a calibrated Instron® tensile tester (model 1130) equipped with a 5000 g load cell, under a continuous strain rate of 5 cm min^{-1} at 25°C. Sample preparation involved drying *in vacuo* at 80°C for 24 h, cooling slowly overnight to room temperature to remove residual stresses, and storage in a desiccator at room temperature until use. Results were recorded as averages of three to five experiments.

Thermal analysis of PEEC and PEEC-TTI networks. Thermal analysis was performed on a DuPont® 9900 thermal analyzer equipped with a 910 differential scanning calorimetry (d.s.c.) cell. Samples (5–20 mg) were dried *in vacuo* at 80°C for 24 h prior to hermetically sealing into aluminium pans. Temperature scans were

performed at a heating rate of 10°C min^{-1} under a constant nitrogen purge.

Characterization

^1H n.m.r. spectra were recorded on a Varian EM-360 (60 MHz for ^1H) or a Bruker model AC-300 spectrometer (300 MHz for ^1H). ^{13}C n.m.r. spectra were recorded on a Bruker model AC-300 spectrometer (75 MHz for ^{13}C).

G.p.c. was performed on a Waters Associates system employing 100, 500, 10^4 and 10^5 Å ultra-styragel columns and a model 410 differential refractometer. Poly(ethylene oxide) (PEO) molecular weight standards were used to obtain a calibration curve.

Vapor phase osmometry (v.p.o.) was performed at 35°C on PEEC samples dissolved in anhydrous 1,2-dichloroethane, using a Knauer no. 11.00 vapour phase osmometer. Calibration solutions of biphenyl in anhydrous 1,2-dichloroethane were prepared over a concentration range of 2–8 g kg^{-1}.

RESULTS AND DISCUSSION

Synthesis of PEEC

The ring-opening polymerization of EC was accomplished using SS as the catalyst and MEG as the initiating species since this system yields nearly perfectly bifunctional, oligomeric diols of high carbonate retention whose molecular weights can be accurately controlled. In addition, compared to other catalysts such as the organotins, SS is less expensive, yields a more rapid polymerization[27] and can be easily removed from the reaction mixture[30]. We have shown that with this system the molecular weight of PEEC can be controlled up to a value of 4600 g mol^{-1} by varying the amount of externally added MEG ($[MEG]_{added}$); molecular weights higher than this are apparently prevented by the presence, in EC monomer, of a prevailing concentration of MEG ($[MEG]_{in\ situ}$)[27,31]. Thus, four large-scale batches of PEEC (~300 g) were produced using external additions of MEG of 0, 1.0, 3.0 and 7.0 mol%. The g.p.c. chromatograms of the four reaction mixtures after ~90% conversion are shown in *Figure 1*. The peak located at

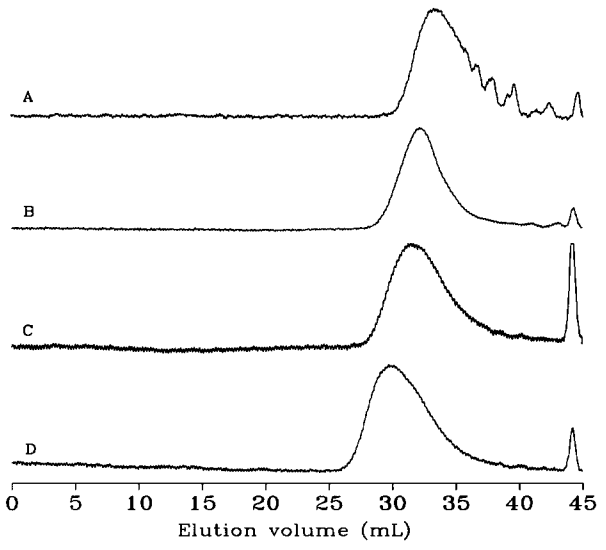

Figure 1 G.p.c. chromatograms of the reaction mixtures after ~90% conversion synthesized with $[MEG]_{added}$ = (A) 7.0, (B) 3.0, (C) 1.0 and (D) 0 mol%

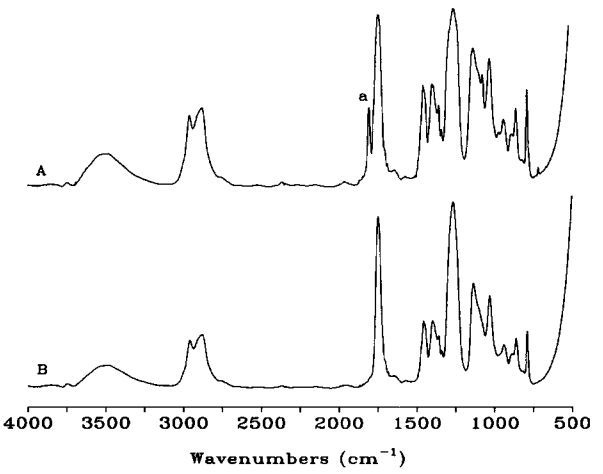

Figure 2 *FT*i.r. absorbance spectra of PEEC oligomer with $\bar{M}_n$ = 1320: (A) immediately following polymerization and (B) following precipitation in methanol

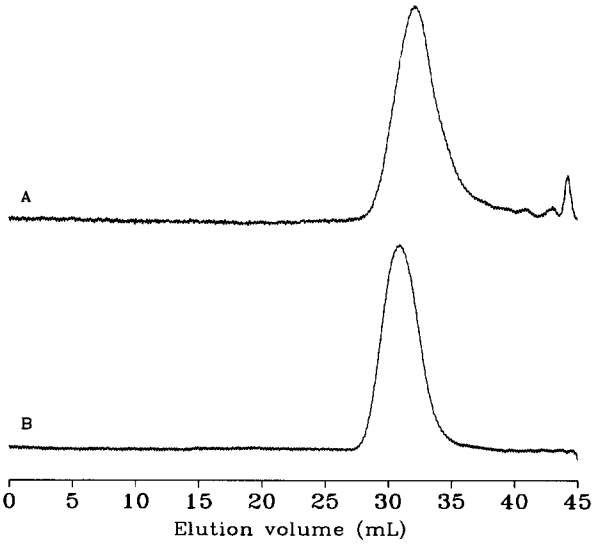

Figure 3 G.p.c. chromatograms of PEEC oligomer with $\bar{M}_n$ = 1320: (A) immediately following polymerization and (B) following precipitation in methanol

~44 ml of elution volume arises from unreacted EC and possibly MEG. The presence of these low molecular weight materials, including diethylene glycol (DEG) which is formed in steady-state concentration throughout the course of the polymerization[25], would have a large effect on the physical properties of derived networks, since unreacted EC would act as an inert plasticizer, raising the sol content, while MEG and DEG would lead to the formation of hard linkages[32]. To remove these impurities the polymerization mixture was precipitated into a 10-fold excess of methanol. We found that the removal of EC can be monitored by following the Fourier transform infra-red (*FT*i.r.) absorbance spectra as shown in *Figure 2*, which depict the PEEC oligomer immediately after reaction (*Figure 2A*) and following precipitation (*Figure 2B*). The presence of the second, narrow carbonyl peak (a) located at 1800 cm^{-1} in *Figure 2A* is due to the carbonyl group in EC, and thus the removal of EC can be monitored by following the disappearance of this peak. It was observed that precipitation not only removed EC, MEG and DEG but also low molecular weight PEEC oligomers (< 500 g). This can be clearly seen in *Figure 3* which shows the g.p.c. chromatograms of PEEC

Table 1 Molecular weight, composition and glass transition temperature of PEEC prepolymers

	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]	CO_2[c] (%)	T_g (°C)
PEEC 730	730	1.78	41.5	−33
PEEC 1320	1320	1.51	44.1	−30
PEEC 2520	2520	1.68	45.3	−27
PEEC 4390	4390	1.54	43.0	−22

[a]Determined from acetylation/titration
[b]Determined from g.p.c.
[c]Determined from ^{1}H n.m.r.

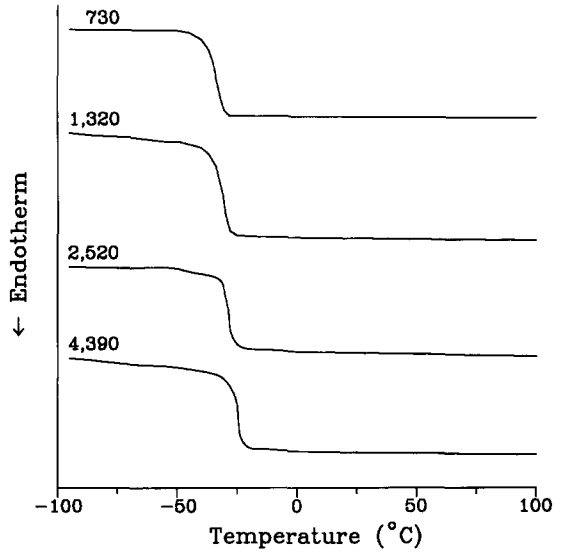

Figure 4 D.s.c. thermograms of the four PEEC oligomers. The numbers above each thermogram are the $\bar{M}_n$ values

oligomer (3.0 mol% MEG added) immediately following polymerization (*Figure 3A*) and after precipitation (*Figure 3B*). In view of this, the reaction mixture synthesized with 7.0 mol% externally added MEG, which was soluble in methanol, was precipitated into H_2O to remove EC, MEG and DEG, followed by drying over anhydrous magnesium sulphate. The removal of low molecular weight material from the samples produced relatively narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.5–1.8) as shown in *Table 1*.

Characterization of PEEC diols

The $\bar{M}_n$, composition and thermal properties of the PEEC prepolymers are listed in *Table 1*. The retention of CO_2 in the four copolymers is relatively high, i.e. ⩾41.0 mol%, suggesting that these materials are essentially alternating copolymers of EO and EC. The thermal properties of the prepolymers were measured by d.s.c.; the thermograms in *Figure 4* illustrate that the incorporation of CO_2 disrupts the ability of the EO units to crystallize ($T_m \sim 60$°C for PEO), and all four prepolymers are completely amorphous. Decreasing the $\bar{M}_n$ of the prepolymers lowers T_g as expected[33]. Values for $\bar{M}_n$ can be obtained via hydroxyl titration ($\bar{M}_{n(OH)}$) by assuming that the PEECs are difunctional. This technique also yields an effective hydroxyl functionality which is the desired quantity for polyurethane synthesis. The $\bar{M}_{n(OH)}$s and the $\bar{M}_n$ values determined by g.p.c. and v.p.o. are shown in *Table 2*. The agreement between the v.p.o. values and the titration values ($\bar{M}_{n(OH)}$) confirms that the prepolymers are difunctional and that the titration method produces hydroxyl numbers representative of the actual hydroxyl concentrations. The agreement between these $\bar{M}_n$ values and those determined by g.p.c. indicate that PEO is a suitable molecular weight standard for PEEC oligomers, which Vogdanis *et al.* also noted[26].

PEEC-TTI network studies

Seven day curing schedule. (1) Network formation. In our early network syntheses, we used TTI as received and employed the following curing cycle: 40°C for 3 days, followed by 2 days at 60°C and finally 2 days at 80°C. (In later syntheses we increased the duration of the final 80°C cure.) It was our objective to estimate the extent of cure by calculating the sol content, i.e. the extractable (unreacted) solids contained within the network and to modify our curing protocol to maximize the extent of cure. The weight lost during solvent extraction of the network, expressed as a percentage of the initial weight is by definition the sol content:

$$\text{Sol content} = \left(\frac{\text{wt}_{\text{initial}} - \text{wt}_{\text{final}}}{\text{wt}_{\text{initial}}}\right) \times 100 \qquad (1)$$

As can be seen in *Figure 5*, the sol content for the networks formed from PEEC 2520 at various PEEC hydroxyl group/TTI isocyanate group (OH/NCO) ratios approached an asymptotic value of 3–4% as the OH/NCO ratio was decreased. This was unexpected

Table 2 Molecular weight characterization of PEEC by various methods

	Number average molecular weight ($\bar{M}_n$)		
	G.p.c.	V.p.o.	Acetylation[a]
PEEC 730	800	–	730
PEEC 1320	1300	–	1320
PEEC 2520	2700	2610	2520
PEEC 4390	4400	4500	4390

[a]PEEC assumed to be difunctional

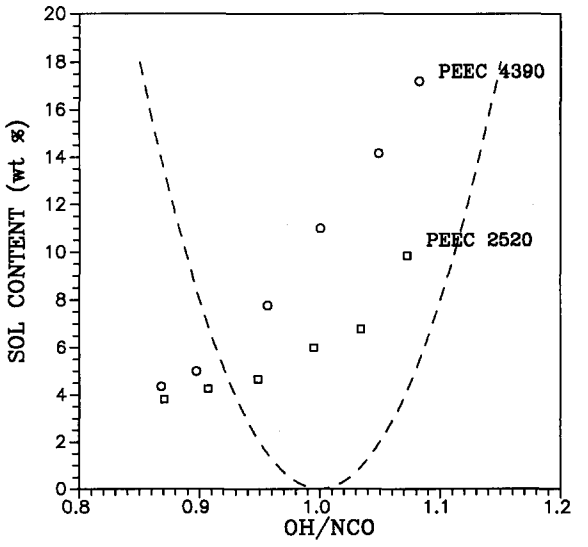

Figure 5 Sol content for the networks cured only 7 days at various OH/NCO ratios. Networks prepared from prepolymers with $\bar{M}_n$ = (○) 4390 and (□) 2520. The broken line indicates theoretically expected behaviour

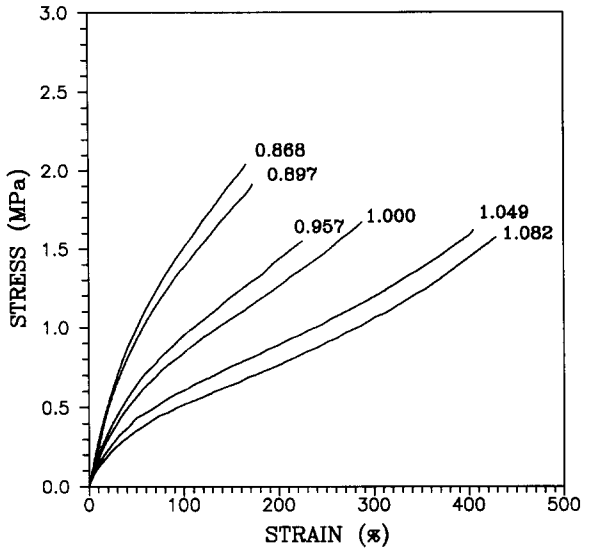

Figure 6 Stress–strain curves for PEEC 4390 networks produced at various OH/NCO ratios. Films were synthesized using TTI as received and the 7 day curing schedule

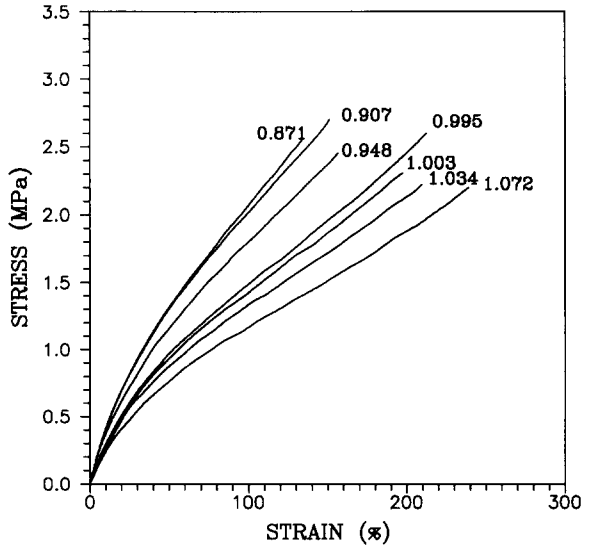

Figure 7 Stress–strain curves for PEEC 2520 networks produced at various OH/NCO ratios. Films were synthesized using TTI as received and the 7 day curing schedule

since upon complete reaction one would expect to see a minimum in sol content centred about the stoichiometric ratio, OH/NCO = 1, as suggested by the broken line in *Figure 5*. The same result was seen for the networks formed from PEEC 4390. In spite of the presence of an appreciable sol content, the extracted films were tack-free and suitable for tensile property measurements.

(2) Tensile properties. In *Figures 6* and *7* are shown the stress–strain curves for networks formed from PEEC 4390 and PEEC 2520, respectively, at a series of OH/NCO ratios. These films were produced using TTI as received and the earlier curing schedule (only 2 days at 80°C). At OH/NCO ratios > 1 a soft rubbery material resulted, and as expected, an increase in isocyanate content led to a tighter network as the stoichiometric ratio was approached. A further excess of isocyanate led to an even stiffer material, probably due to an increase in the extent of cure between the hydroxyl groups on PEEC and the isocyanate moieties of TTI. This is reasonable since at low OH/NCO ratios, the overall molar concentration of all functional groups is higher and the sol content results show that at OH/NCO = 1 the networks are not fully cured after 7 days. It is possible that higher OH/NCO ratios lead to some condensation between TTI moieties, e.g. allophanate or isocyanurate formation.

(3) Extraction and swelling. The procedure for measuring the molecular weight between crosslinks, $\bar{M}_c$, of the networks by an equilibrium swelling technique is complicated by having to first determine a χ interaction parameter[34] for the solvent–network system, which is present in the literature only for a few select polymer–solvent pairs[35]. In the absence of χ, we were interested in using equilibrium swelling as a qualitative tool for comparing crosslink density. We chose 1,2-dichloroethane as the swelling solvent since during extraction studies it was shown to readily swell PEEC networks.

Since TTI is exactly trifunctional, at complete reaction of a perfectly stoichiometrically balanced network, the $\bar{M}_c$ is equal to the $\bar{M}_n$ of the PEEC prepolymer plus two-thirds the molecular weight of TTI. To compare the crosslink densities of the networks, a value for χ can be estimated from the swelling data by substituting this value for $\bar{M}_c$ into equation (2)[36]:

$$\bar{M}_c = \frac{\bar{V}_1 \rho_2 \left(V_2^{1/3} - \frac{V_2}{2} \right)}{-[\ln(1 - V_2) + V_2 + \chi V_2^2]} \qquad (2)$$

In equation (2) $\bar{V}_1$ is the molar volume of 1,2-dichloroethane, ρ_2 is the network density and V_2 is the equilibrium volume fraction of polymer in the swollen network. In our early studies we were unable to produce networks with low sol content, and thus due to the error involved in estimating χ from equation (2) at high sol contents, we chose not to use $\bar{M}_c$ as a device for comparing crosslink densities of the earlier networks. Instead we simply compared the equilibrium volume fraction of polymer in the swollen networks, V_2, as calculated according to equation (3):

$$V_2 = \left(\frac{w_o}{V_{equil} \times \rho_2} \right) \qquad (3)$$

where w_o is the initial weight of the network and V_{equil} is the equilibrium volume of the swollen network, which is defined in equation (4), assuming additivity of volumes, where w_s is the weight of the swollen network and ρ_1 is the density of 1,2-dichloroethane.

$$V_{equil} = \left(\frac{w_o}{\rho_2} \right) + \left(\frac{w_s - w_o}{\rho_1} \right) \qquad (4)$$

The initial swelling studies involved the two series of networks, PEEC 4390 and 2520, which were cured employing only a 2 day curing cycle at 80°C. The results are shown in *Tables 3* and *4* for PEEC 4390 and 2520, respectively. The equilibrium volume fraction of polymer in the swollen network was observed to increase as the OH/NCO ratio was decreased, which agrees with the sol content values, shown in *Figure 5*, and the tensile properties shown in *Figures 6* and *7*. These results suggest that the observed increase in crosslink density results from an increase in cure (urethane formation) and not

Table 3 Equilibrium swelling results for networks formed from PEEC 4390 (7 day curing schedule)

OH/NCO	Density (g cm^{-3})	Weight gain (%)	V_1[a]	V_2[b]
1.082	1.188	725	0.873	0.127
1.049	1.178	698	0.866	0.134
1.000	1.198	567	0.844	0.156
0.957	1.186	488	0.822	0.178
0.897	1.186	405	0.793	0.207
0.868	1.204	389	0.789	0.211

[a] V_1 is the volume fraction of 1,2-dichloroethane
[b] V_2 is the volume fraction of PEEC 4390 network

Table 4 Equilibrium swelling results for networks formed from PEEC 2520 (7 day curing schedule)

OH/NCO	Density (g cm^{-3})	Weight gain (%)	V_1[a]	V_2[b]
1.034	1.198	341	0.766	0.234
1.003	1.210	337	0.765	0.235
0.995	1.200	331	0.760	0.240
0.948	1.201	299	0.741	0.259
0.907	1.195	288	0.733	0.267
0.871	1.182	274	0.721	0.279

[a] V_1 is the volume fraction of 1,2-dichloroethane
[b] V_2 is the volume fraction of PEEC 2520 network

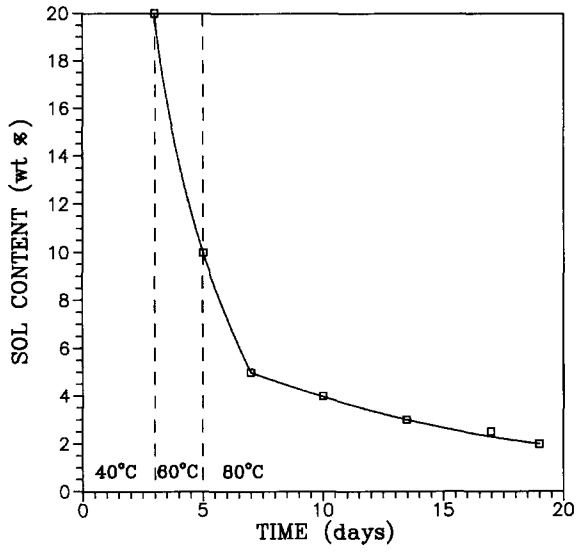

Figure 8 Sol content for a PEEC 2520 network (OH/NCO = 1) *versus* curing time

from a high incidence of condensation between isocyanate groups.

Seventeen day curing schedule. (1) Network formation. To investigate the relatively high sol contents of these networks, we used purified TTI and examined the effect of curing time on sol content. As can be seen in *Figure 8*, the sol content for a PEEC 2520 network formed with TTI decreased with increased curing time until a sol content of ~2 wt% was attained after 19 days, which suggested that the previously observed high sol contents were due to incomplete reaction and were *not* caused by imbalances in the stoichiometry. To produce low sol content networks routinely, we modified the curing procedure by extending the 80°C stage from 2 to 14 days, which decreased the sol content of the OH/NCO = 1 networks to ~2–5 wt%, which we considered to be acceptable. The effect of the curing time extension on the sol content at various OH/NCO ratios for the networks produced with the four PEEC prepolymers is shown in *Figure 9*. In all cases acceptable (<5 wt%) sol contents resulted with the minimum sol content centred about OH/NCO = 1. The apparent inability to achieve even lower sol contents, say <2 wt%, could possibly be due to the nature of the hard (TTI) core, which for steric reasons may possess a lower reactivity of the third isocyanate group after reaction of the other two[37]. The extended curing schedule also produced tack-free networks which were acceptable for tensile testing.

(2) Tensile properties. Extension of the final curing stage to 14 days not only affected the sol content but drastically altered the final mechanical properties of the network. The stress–strain curves for the networks produced from PEEC 4390, 2520, 1320 and 730 at various OH/NCO ratios and using the extended cure schedule are shown in *Figures 10–13*. As was seen before, as the stoichiometric ratio was approached, an increase in isocyanate content led to a tighter network. A further excess of isocyanate over the stoichiometric ratio led to a stiffer material even though the sol content was higher. Now, it would seem that stiffening of the network as OH/NCO decreases is clearly due to side reactions between isocyanate groups (allophanate and isocyanurate formation), but the question arises whether the side reactions are kinetically competitive with urethane formation only toward the latter stages of the cure, i.e. after gelation and accompanying loss of mobility, or are kinetically competitive throughout the entire network-forming reaction. For the second case, it would be anticipated that sol contents would be increased especially at OH/NCO > 1 since the side reactions would consume isocyanate groups and further magnify the initial stoichiometric imbalance. In addition for the

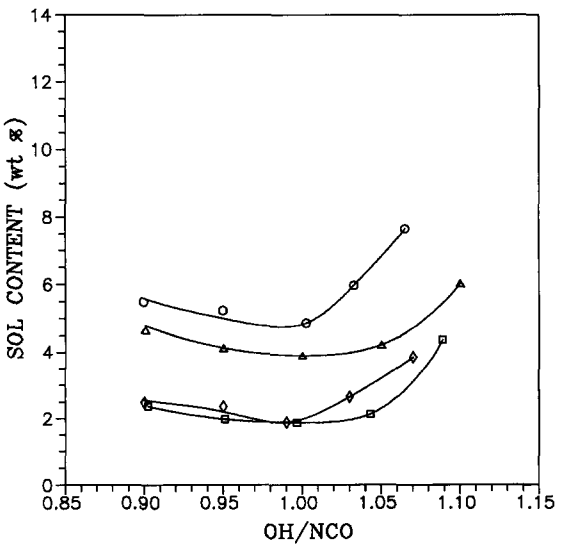

Figure 9 Effect of extended curing schedule (17 days) on the sol content of the networks at various OH/NCO for the networks produced with the four PEEC prepolymers of $\bar{M}_n$ = (○) 4390, (□) 2520, (◇) 1320 and (△) 730

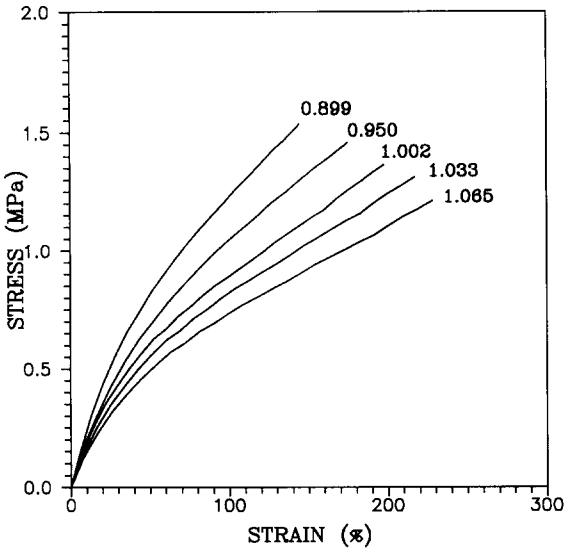

Figure 10 Stress–strain curves for PEEC 4390 networks produced at various OH/NCO ratios. Films were synthesized using purufied TTI and the 17 day curing schedule

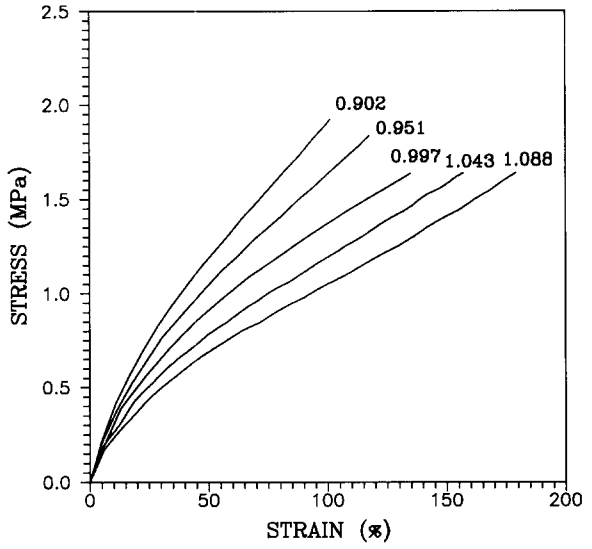

Figure 11 Stress–strain curves for PEEC 2520 networks produced at various OH/NCO ratios. Films were synthesized using purified TTI and the 17 curing schedule

second case, the sol content *versus* OH/NCO curves would not be expected to necessarily possess a minimum at a ratio of 1. Since a minimum in the sol content does occur at OH/NCO = 1 and relatively low sol contents result ($\leqslant 5$ wt%) at high OH/NCO ratios, we suggest that side reactions are competitive only at the latter stages of the curing reaction. In fact, studies of the reaction of isocyanates with alcohols and urethane linkages have shown that urethane formation occurs preferentially over the side reactions[38,39].

The network stiffening trend which occurs with decreasing OH/NCO ratios may be clearly seen in *Figures 14* and *15* where the effect of OH/NCO on the modulus and strain at break, respectively, of the networks is shown. Although the plots may or may not be linear, unquestionably a definite trend was observed. It is interesting to note that the strain at break for the networks synthesized with PEEC 730 were consistently higher than those of PEEC 1320. This was somewhat unexpected since the networks with the higher molecular weight prepolymers should be softer and should break at higher strains. The observed effect, however, is apparently due to the changing chemical composition of the networks brought about by the stoichiometric demand for greater triisocyanate content at lower PEEC molecular weight. For example, the PEEC 730 network synthesized at OH/NCO = 1, consists of only 75.0% PEEC (w/w) compared to 84.4%, 91.2% and 94.7% (w/w) for PEEC 1320, 2520 and 4390, respectively. Apparently for PEEC 730, TTI physically comprises such a substantial volume fraction of the network, that the network begins to display some characteristics of an aromatic polyurethane network, which one might envisage to be extremely strong and tough. This low molecular weight sample however, does not produce a composition where the network becomes brittle as was found for polyisobutylene-TTI networks[40].

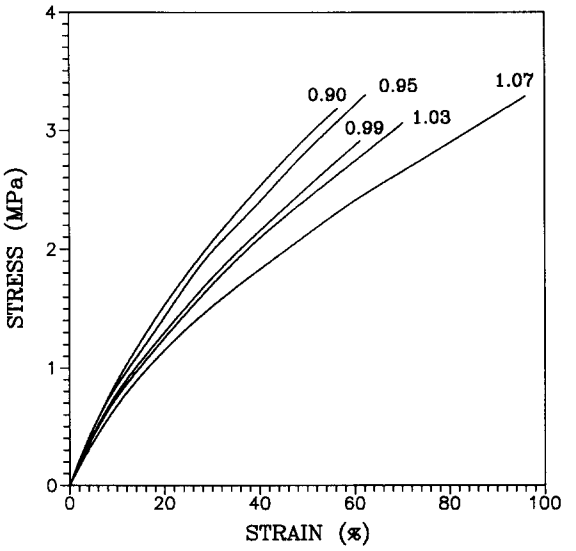

Figure 12 Stress–strain curves for PEEC 1320 networks produced at various OH/NCO ratios. Films were synthesized using purified TTI and the 17 day curing schedule

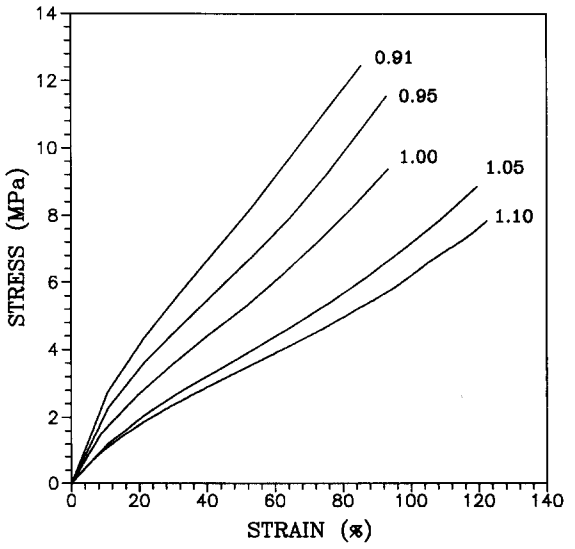

Figure 13 Stress–strain curves for PEEC 730 networks produced at various OH/NCO ratios. Films were synthesized using purified TTI and the 17 day curing schedule

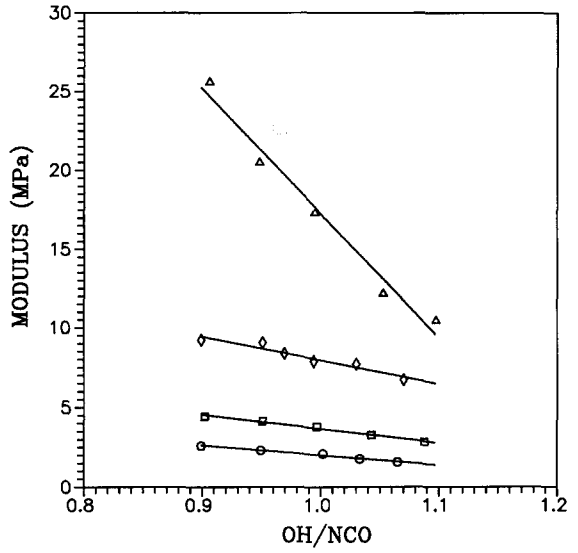

Figure 14 Effect of the OH/NCO ratio on the modulus of the PEEC-TTI networks cured using the 17 day schedule. Networks prepared from prepolymers with $\bar{M}_n$ = (○) 4390, (□) 2520, (◇) 1320 and (△) 730

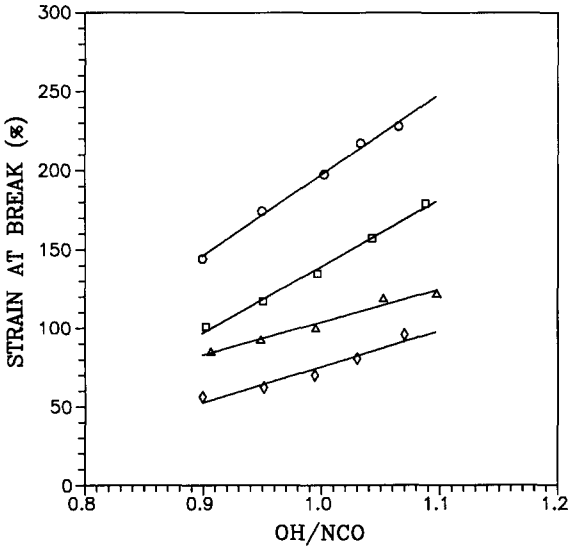

Figure 15 Effect of the OH/NCO ratio on the strain at break of the PEEC-TTI networks cured using the 17 day schedule. Networks prepared from prepolymers with $\bar{M}_n$ = (○) 4390, (□) 2520, (◇) 1320 and (△) 730

The stress–strain curves for the four PEEC prepolymers at stoichiometry (OH/NCO = 1) are shown in *Figure 16*, and the results of their tensile properties are listed in *Table 5*. Since a true trifunctional isocyanate was employed, M_c can be assumed to be approximately equal to the $\bar{M}_n$ of the PEEC prepolymer used plus two-thirds the molecular weight of TTI. As expected, the network became softer and more rubbery, characterized by decreased modulus and ultimate strength, while the strain at break increased, with increasing $\bar{M}_n$ of the prepolymer ($\bar{M}_c$ of the network). It is generally considered that the area under the stress–strain curve is proportional to toughness, and it is clear that the lower the $\bar{M}_n$ of the PEEC prepolymer the tougher the resultant network. It is also interesting to note that compared to the PEEC 2520 network, the tensile properties of the PEEC 1320 network are lower than those which might be expected from decreasing by one-half the $\bar{M}_n$ of the PEEC prepolymer. This observation may reflect a contribution of TTI to the tensile properties of the PEEC 1320 networks, as was discussed above for PEEC 730 networks.

(3) Extraction and swelling. Since we were able to produce low sol content networks using the extended curing schedule, we returned to equation (2) to estimate a value for χ from the swelling data. Referring to *Table 5*, the network produced from the PEEC oligomer of $\bar{M}_n$ = 2520 had a low sol content of 1.8% suggesting that in this case network formation occurred almost completely. Thus the $\bar{M}_c$ of this network should be approximately equal to that calculated theoretically, i.e. $\bar{M}_c$ should be equal to the $\bar{M}_n$ of the prepolymer plus two-thirds of the molecular weight of TTI. This results in a theoretical $\bar{M}_c$ = 2800. Substituting this value into equation (2), we arrived at an estimated value for χ of 0.34 which indicates that 1,2-dichloroethane is a strong swelling solvent for this network, since good solvents[41] for a polymer typically have $\chi \leqslant 0.5$. Referring again to *Table 5*, the network produced from the PEEC oligomer of $\bar{M}_n$ = 1320 also had a sol content of 1.8%, and the approach outlined above yields a theoretical $\bar{M}_c$ = 1500. Upon substitution of this value into equation (2), the χ value was calculated to be 0.45. The discrepancy between these two χ values is no doubt due to differences in composition of the two networks, i.e. the network produced from the smaller PEEC prepolymer will possess more aromatic urethane character. Due to the differences in the calculated χ values we again chose to use V_2 rather than $\bar{M}_c$, as a device for comparing crosslink densities of the networks.

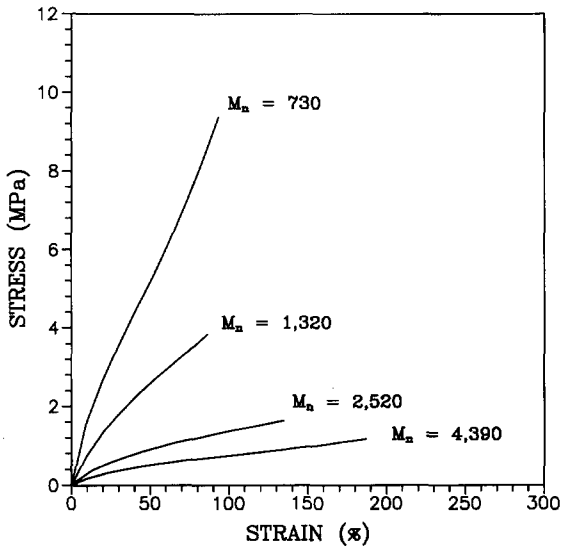

Figure 16 Stress–strain curves for the four PEEC networks produced at stoichiometry (OH/NCO = 1) and cured using the 17 day schedule

Table 5 Tensile properties of PEEC networks at OH/NCO = 1:1

$\bar{M}_{n(OH)}$	Sol content (%)	Modulus (MPa)	Strain at break (%)	Tensile strength (MPa)
730	4.0	17.55	93	9.37
1320	1.8	7.80	86	3.83
2520	1.8	4.05	137	1.64
4390	4.8	2.15	186	1.17

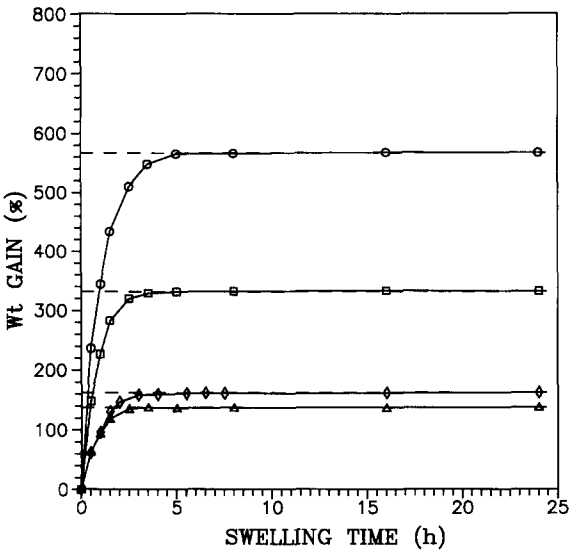

Figure 17 Effect of swelling time on the weight gain for the four PEEC networks at an OH/NCO ratio = 1. Networks prepared from prepolymers with $\bar{M}_n$ = (○) 4390, (□) 2520, (◇) 1320 and (△) 730

Table 6 Equilibrium swelling results for networks formed from PEEC 4390 (17 day curing schedule)

OH/NCO	Density (g cm^{-3})	Weight gain (%)	V_1[a]	V_2[b]
1.065	1.198	644	0.860	0.140
1.033	1.217	577	0.848	0.152
1.002	1.201	517	0.832	0.168
0.950	1.216	456	0.816	0.184
0.899	1.221	382	0.788	0.212

[a] V_1 is the volume fraction of 1,2-dichloroethane
[b] V_2 is the volume fraction of PEEC 4390 network

Table 7 Equilibrium swelling results for networks formed from PEEC 2520 (17 day curing schedule)

OH/NCO	Density (g cm^{-3})	Weight gain (%)	V_1[a]	V_2[b]
1.088	1.214	345	0.770	0.230
1.043	1.220	322	0.759	0.241
0.997	1.212	301	0.744	0.256
0.951	1.218	279	0.730	0.270
0.902	1.224	258	0.716	0.284

[a] V_1 is the volume fraction of 1,2-dichloroethane
[b] V_2 is the volume fraction of PEEC 2520 network

The effect of swelling time on the weight gain:

$$\text{Weight gain (\%)} = \left(\frac{w_s - w_o}{w_o}\right) \times 100 \qquad (5)$$

was examined for the four PEEC networks cured using the extended schedule and at an OH/NCO ratio = 1. The results are shown in *Figure 17*. In all cases the equilibrium weight gain was attained after ~12 h; however, to ensure accuracy of the equilibrium values, weight gain data were collected every 24 h for at least 5 days, and then an average value was recorded.

The results of the equilibrium swelling for the networks synthesized at the longer cure schedule (14 days at 80°C) are shown in *Tables 6*, *7*, *8* and *9* for PEEC 4390, 2520, 1320 and 730, respectively. An increase in isocyanate content also resulted in a decrease in V_2, suggesting a higher crosslink density at lower OH/NCO ratios. This result, coupled with the earlier tensile properties and sol content data, supports our earlier conclusion that for PEEC networks cured at the more rigorous schedule, stiffening at higher isocyanate content results mostly from side reactions, such as allophanate or isocyanurate formation, that occur after the bulk of the urethane (network) formation has taken place (case 1), and not from an increase in the extent of cure.

(4) Thermal analysis of PEEC networks. Glass transition temperature of the four series of PEEC-based networks synthesized at the extended curing schedule are shown in *Figure 18*. As expected, the network T_gs increase with decreasing PEEC prepolymer molecular weight.

Table 8 Equilibrium swelling results for networks formed from PEEC 1320 (17 day curing schedule)

OH/NCO	Density (g cm^{-3})	Weight gain (%)	V_1[a]	V_2[b]
1.070	1.248	174	0.634	0.366
1.030	1.236	173	0.630	0.370
0.994	1.230	162	0.614	0.386
0.951	1.225	154	0.601	0.399
0.899	1.225	152	0.598	0.402

[a] V_1 is the volume fraction of 1,2-dichloroethane
[b] V_2 is the volume fraction of PEEC 1320 network

Table 9 Equilibrium swelling results for networks formed from PEEC 730 (17 day curing schedule)

OH/NCO	Density (g cm^{-3})	Weight gain (%)	V_1[a]	V_2[b]
1.098	1.228	159	0.609	0.391
1.053	1.227	148	0.592	0.408
0.995	1.241	137	0.576	0.424
0.948	1.206	126	0.548	0.452
0.906	1.212	120	0.537	0.463

[a] V_1 is the volume fraction of 1,2-dichloroethane
[b] V_2 is the volume fraction of PEEC 730 network

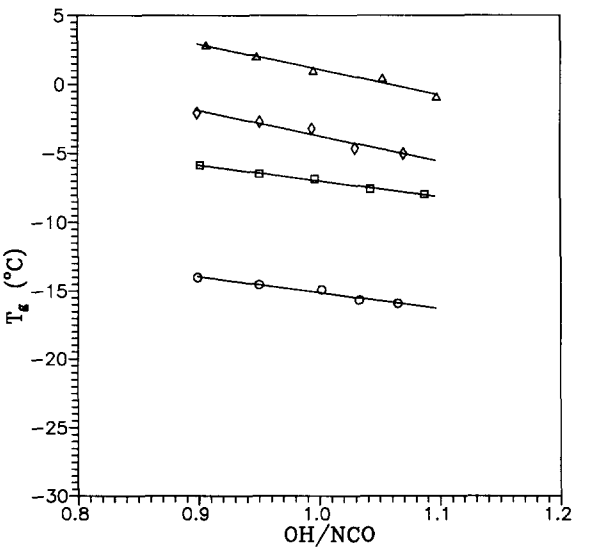

Figure 18 Effect of the OH/NCO ratio on the T_g of the four series of PEEC-TTI networks synthesized using the 17 day curing schedule. Networks prepared from prepolymers with $\bar{M}_n$ = (○) 4390, (○) 2520, (◇) 1320 and (△) 730

Upon examining the effect of curing stoichiometry on T_g, we observed a definite trend of increasing T_g with increasing isocyanate content. This result again supports our claim that at the more rigorous curing schedule, excess isocyanate groups lead to side reactions, which tend to increase the crosslink density and thus increase the T_g of the network, only after the majority of urethane formation has occurred.

CONCLUSIONS

EC may be readily polymerized using MEG as initiator and SS as heterogeneous catalyst, to produce useful, hydroxy-terminated PEEC soft segments which may be used to synthesize polyurethane thermoplastic and network polymers. These diol prepolymers are of special interest as propellent binders due to their relatively high O_2 content; however, PEEC diols produced under these conditions retain, at best, only 50 mol% of the carbonate residues so that the polymer structure is composed of alternating EO and EC units (with di- and higher PEO units present in prepolymers which display <50 mol% carbonate retention). Addition of varying amounts of MEG to the polymerization allows for accurate control of molecular weight for $\bar{M}_n \leqslant 4600$, but molecular weights higher than this are not easily achieved due presumably to a prevailing concentration of MEG which is present in EC monomer.

The purified polymers of this study were found to be hydroxy-terminated by comparison of equivalent weights determined by acetylation/titration and $\bar{M}_n$ values from v.p.o. measurements, and they were determined to be amorphous with the observed T_g decreasing with increasing $\bar{M}_n$ of the prepolymer. The primary hydroxyl end groups reacted readily with aromatic isocyanates, and a series of four networks were produced from the reaction of four different molecular weight PEEC diols with a trifunctional isocyanate (TTI). A network curing schedule of 7 days produced networks with high sol contents that approached an asymptotic value of 4 wt% as the OH/NCO ratio was decreased. Extension of the curing schedule to 19 days (14 days at 80°C) produced networks with low sol contents, 2–5 wt%, with the minimum sol content centred about a stoichiometric ratio (OH/NCO ~ 1). At increased isocyanate contents, tensile properties, equilibrium swelling and T_g measurements indicated that crosslink density of the networks was higher possibly due to side reactions between urethane linkages and remaining isocyanate groups resulting in allophanate formation; however, because sol contents remained relatively low even at high OH/NCO ratios, these reactions probably only occur at the very latest stages of the reaction. Under stoichiometric curing conditions, the networks became softer and more rubbery, characterized by decreasing modulus and ultimate strength, and increasing strain at break, as the $\bar{M}_n$ of the prepolymer was increased.

Swelling experiments with the networks showed that a unique polymer–solvent interaction parameter, χ, could not be specified for this series of networks. Because of the low molecular weights of the primary diol chains, stoichiometric considerations caused the various networks to possess quite different aromatic urethane contents. Of course, as the primary chain molecular weight increases the interaction parameter must approach an asymptotic value indicative of the interactions of pure PEEC chains with the swelling solvent. For 1,2-dichloroethane, this value would appear to be <0.34, indicating that this solvent is a very good one indeed for PEEC networks but becomes poorer the higher the aromatic urethane content of the network.

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