

Hydrogenated hydroxy-terminated polyisoprene (HHTPI) based urethane network: network properties

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Abstract

Polyurethane (PU) networks based on hydrogenated hydroxytelechelic polyisoprene (HHTPI) and isophorone diisocyanate isocyanurate (IIPDI) were prepared and studied. Determination of the critical conversion point ($p_c=0.58$) was obtained experimentally through rheological measurements. This value was similar to the value predicted using the Macosko Miller model. Differential scanning calorimetry (DSC) analyses show that PUs with a high degree of phase separation is obtained (81% for $[\text{NCO}]/[\text{OH}]=1$). This phase segregation decreased when hard segment content increased. Glass transition temperature of the soft segment, $T_{gs} = -66^\circ\text{C}$, was little affected by hard segment content. Thus, the resulting polyurethanes exhibit elastomeric properties.

For $[\text{NCO}]/[\text{OH}]>1$ ratios, a second transition at 70°C was observed and attributed to hard segment interactions. Using swelling measurements, the solubility parameter δ , polyurethane–THF interaction parameter (χ), crosslink densities (ν_c) and the molecular weight between crosslinks (\bar{M}_c) were determined.

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1. Introduction

Segmented polyurethanes consisting of alternating soft (low glass transition) and hard segments are one of the most frequently investigated polymers due to their wide range of properties [1]. Adhesives, protective coatings, biomaterials, and high performance elastomers are among the fields where these polymers find application. Availability of a very large selection of reactants (diisocyanate, chain extender, diol oligomer) leads to the preparation of a wide variety of segmented polyurethanes, each having specific properties. Among the various diol oligomers (soft segment), such as polyester, polyether, polycarbonate, polysiloxane or polyacrylate, hydrocarbon types exhibit very interesting properties. The most well known are hydroxytelechelic polybutadiene (HTPB)-based polyurethanes, which find their major application in propellant binders [2]. In the past decade, hydrogenated hydrocarbon diol

oligomers have been investigated. Compared to their corresponding unsaturated homologues, the inertness of these soft segments contribute to enhance solvent resistance, as well as hydrolytic, oxidative, thermal and mechanical properties of the resulting segmented polyurethanes [3,4–7]. This excellent combination of properties makes these materials of interest for automobile manufacture, coatings and electrical insulation applications [8].

In a previous study we followed the condensation reaction between a hydrogenated hydroxytelechelic polyisoprene (HHTPI) and isophorone diisocyanate isocyanurate (I-IPDI) using FTIR spectroscopy [9]. Reaction kinetics were studied using FTIR and the rates of individual isocyanate groups could be described by a second order equation. According to the functionalities of the reactants, both greater than two, PU networks were obtained.

In the present work theoretical modelling of the network was attempted using the model developed by Macosko and Miller [10,11]. Calculated values of the critical conversion (gelation point), p_c , for stoichiometric conditions were compared to experimental values obtained by rheological

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measurements. Network structure–properties relationships were analyzed. The influence of hard segment content on thermal and mechanical properties, as well as phase separation was checked. Molecular weight between cross-links, \bar{M}_c , was determined by swelling measurements.

2. Experimental

2.1. Materials

HHTPI (EPOL[®] Atofina, $\bar{M}_n = 2700$, $I_{OH} = 0.92$ mequiv. g^{-1}) and IPDI isocyanurate (VESTANAT[®] 1890/100, Degussa–Hüls, $\bar{M}_n = 825$, $16 \pm 1\%$ NCO w/w) were kindly supplied. Dibutyltin dilaurate (DBTL), cyclohexylisocyanate, *n*-heptanol (Aldrich) and freshly distilled tetrahydrofuran (THF) were used.

2.2. Synthesis

HHTPI was introduced in a 250 ml round bottom flask equipped with a mechanical stirrer (300 rpm), a switchable inlet for nitrogen and a vacuum connector. HHTPI was degassed for 1 h under vacuum (10^{-2} mmHg) at room temperature and then placed in a nitrogen atmosphere. DBTL was added in the desired amount, as well as the isocyanurate previously dissolved in THF (50% w/w). Ratios $r = [NCO]/[OH]$ between 0.5 and 2.2 were studied. After 10 min stirring, the reaction media was cast in teflon moulds and allowed to dry at room temperature for 7 days. Transparent, colourless films were obtained.

2.3. Differential scanning calorimetry (DSC) of PU films

Glass transition temperatures, T_g , of the polyurethane samples were determined by differential scanning calorimetry (DSC 7 Perkin–Elmer). Temperature scans were carried out under N_2 atmosphere from -85 to -30 °C and from 35 to 100 °C with a heating rate of 20 °C/min. Standard calibration was performed with *n*-decane ($T_m = -50$ °C) and indium ($T_m = 156.6$ °C). T_g was determined as the midpoint value.

2.4. PU swelling in THF

Swelling measurements were performed at room temperature in THF. After weighing, swelled samples (m_s) were dried at 60 °C until a constant mass was obtained (m_d). Swelling (Q_s) was then calculated using the following equation:

$$Q_s = 1 + \frac{\rho_p}{\rho_0} \frac{m_s - m_d}{m_d} \quad (1)$$

where ρ_p and ρ_0 are polyurethane and THF density, respectively.

2.5. Rheological characterization

Rheological measurements, which were performed to determine sol–gel transition and dynamic viscoelastic properties, were carried out using a Carri Med CSL 100 (Rheo) controlled stress rheometer fitted with a Peltier temperature control device. The linearity of viscoelastic properties was investigated before the measurements of storage (G') and loss (G'') moduli. A double concentric cylinder measuring geometry was used, (plate/plate 6 or 2 cm). All multiwave measurements were run with frequencies ranging from 0.1 to 15 Hz in bulk at 70 °C without catalyst and with a fixed strain of $\gamma = 2\%$.

3. Results and discussion

3.1. Rheological characterizations

HHTPI precursor structures contain 88/6/6% of 1,4, 1,2 and 3,4-isoprene units, respectively [12], and lead to four identified primary alcohol end groups after hydrogenation [13]. We showed in a recent work that the different hydroxyl functions present on HHTPI could be considered to be equireactive and independent [9]. The structural study of IPDI isocyanurate (I-IPDI), shows that primary and secondary isocyanate groups are present in a 33/67 ratio (primary/secondary) [14], with each isocyanate group exhibiting different reactivities [9].

Theoretical modeling of the step-reaction polyurethane network was achieved using Macosko Miller model, which assumes that (i) the functional groups react independently, (ii) no side reactions occur and (iii) reactivities of all functional groups of a given type have the same reactivity. Although I-IPDI isocyanate groups exhibit different reactivities, the model was used to predict the gelation point since our goal was to estimate the beginning of the reticulation process and to compare it to the experimental gel point. The critical conversion (gelation point), p_c , was therefore determined for the stoichiometric reaction using Eq. (2):

$$rp_c^2 = \frac{1}{(\bar{f}_{wOH} - 1)(\bar{f}_{wNCO} - 1)} \text{ with } r = \frac{[NCO]}{[OH]} = 1 \quad (2)$$

\bar{f}_{wNCO} and \bar{f}_{wOH} are I-IPDI and HHTPI average weight functionality, respectively. The values of \bar{f}_{wOH} is unknown but can be roughly assimilated to $\bar{f}_{nOH} = 2.34$. Thus, as $\bar{f}_{wNCO} = 3.43$ [9], a value of $p_c \sim 0.55$ is obtained.

Experimental gel point was determined using rheological measurements. In the initial part of the reaction, before gelation, the system has the characteristic feature of a Newtonian liquid, where G'' is greater than G' . After gelation, the network has a predominantly elastic character and G' is greater than G'' . Generally, the gel point is considered as the time required for G' and G'' to be identical

[15,16]. According to Fig. 1, which illustrates variations of G' and G'' with applied frequencies at different reaction times, the gel time is roughly 330 min.

Another, more accurate, definition of the gel point was given by Winter et al. as the point where $\tan\delta$, the ratio of G'' to G' , is independent of frequency [17,18].

The dynamic mechanical behaviour at the gel point is given by a power law relation between complex modulus G^* and the angular frequency (ω): $G^* = G'(\omega) + iG''(\omega) = (i\omega)^n$, where $G'(\omega)$ is the real part, or storage modulus, and $G''(\omega)$ is the imaginary part, or loss modulus. This gives $G'(\omega) \sim G''(\omega) \sim \omega^n$. Consequently, the loss angle at the gel point (δ_c) is proportional to the relaxation exponent and independent of frequency:

$$\delta_c = n \frac{\pi}{2} \quad \text{or} \quad \tan \delta_c = \tan\left(n \frac{\pi}{2}\right) \quad (3)$$

The gel point corresponding to the sol–gel transition is the critical point at which the $\tan \delta$ curves versus $f(\omega, t)$ intersect [19,20] (Fig. 2). This time point, $t_c = 330$ min, corresponds to a critical conversion of $0.58 < p_c < 0.59$ according to the FTIR kinetic study (Fig. 3).

At the gel point, $\tan(\delta_c)$ was found to equal 1.4, which corresponds to a relaxation exponent of $n = 0.6$ according to Eq. (3). This result is in accordance with the literature for polyurethane systems [20–22] and intermediate to the percolation ($n = 2/3$) and classic ($n = 0.5$) predictions. As reported by Winter et al. for $n > 0.5$, we also observed that the gel point preceded the intersection of G' and G'' ($\tan \delta = 1$).

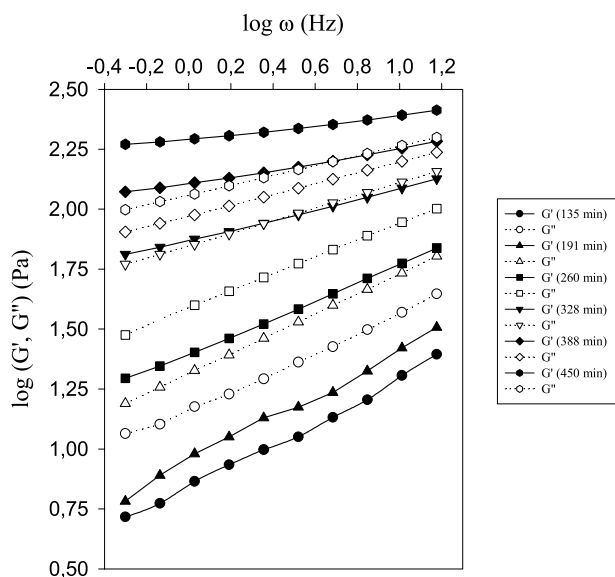


Fig. 1. Dynamic storage (G') and loss (G'') moduli values (respectively, filled and empty symbols) versus $\log \omega$ at different reaction times for the bulk reaction between HHTPI and I-IPDI at 70 °C without catalyst (●: 135, ▲: 190, ■: 260, ▼: 330, ◆: 390, ○: 450 min).

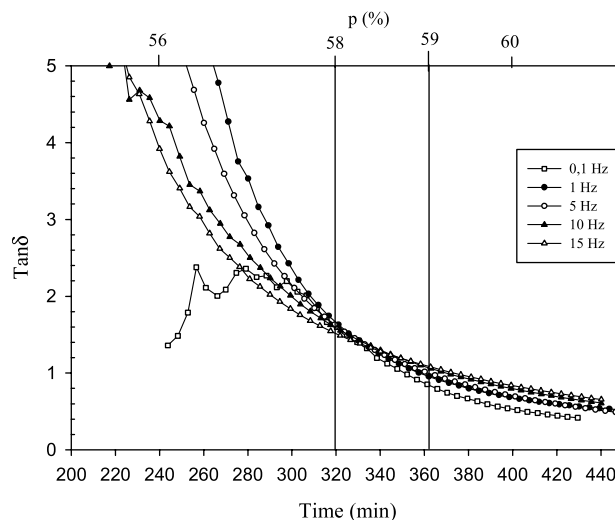


Fig. 2. $\tan \delta$ curves versus time for frequencies ranging from 0.1 to 15 Hz with fixed strain of $\gamma = 2\%$.

3.2. Transition temperatures and network relaxations

DSC and swelling measurements were used to establish structure–properties relationships and to determine the hard soft segment segregation in the HHTPI-based polyurethane network.

Highly segmented polyurethanes have soft segments exhibiting a low glass transition temperature. This is generally minimally affected by hard segment content, which may also exhibit a distinct thermal transition [23–28]. It is generally accepted that this phenomenon is linked to thermodynamic incompatibility between hard and soft segments.

Camberlin et al. [30] showed that it is possible to quantitatively evaluate soft segment segregation rate by DSC measurements for linear segmented polyurethanes. They defined the soft-phase segregation rate, or degree of phase separation (DPS), as $\xi = \Delta C_p / \Delta C_p^0$ where ΔC_p^0 is the

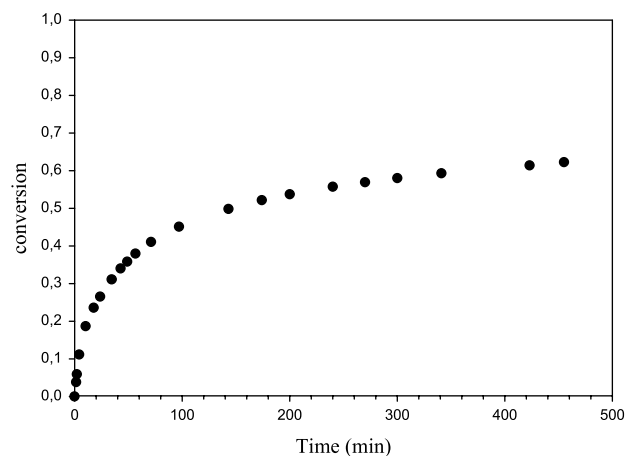


Fig. 3. Conversion versus time of the bulk reaction at 70 °C of HHTPI/I-IPDI [9].

specific heat capacity change at the glass transition of the starting polyol, i.e. pure soft segment, and ΔC_p is the specific heat capacity change at the glass transition of the soft segment in the polyurethane. For values of ξ close to 1, it is believed that few interactions between soft and hard segments occur. Phase segregation is optimum when soft segments are in the soft phase and likewise for the hard

segments. For $\xi < 1$, a portion of the soft segments lie outside the soft phase. These dispersed soft segments do not relax at the same temperature as the continuous soft phase, leading to values of ΔC_p lower than ΔC_p^0 .

Polyurethanes having different soft–hard segment contents ($0.5 < r = ([\text{NCO}]/[\text{OH}]) < 2.2$) were first analyzed by DSC. Enthalpy curves are presented in Fig. 4(a) and (b).

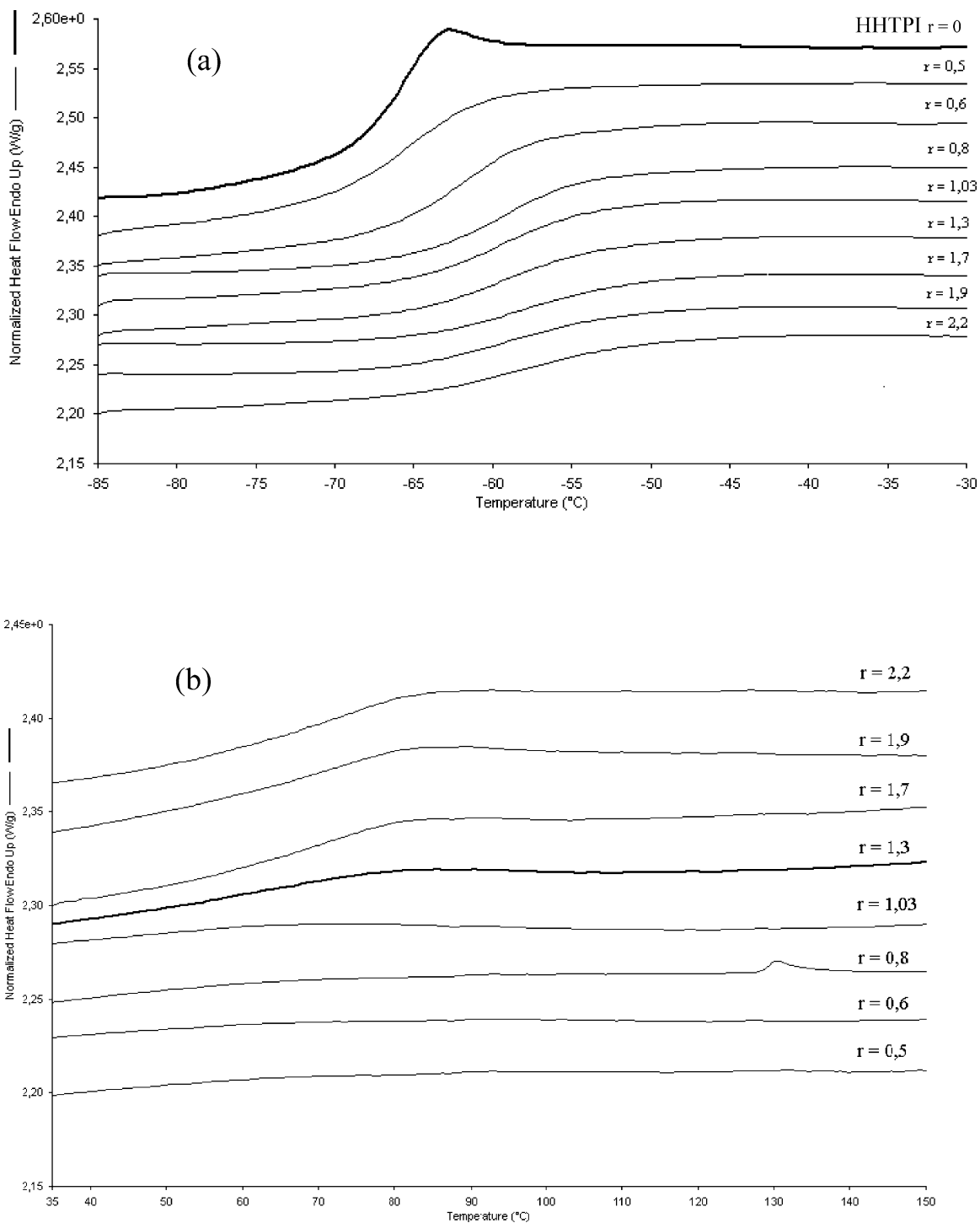


Fig. 4. DSC thermograms of HHTPI/IPDI polyurethanes for different NCO/OH ratios, under nitrogen at a scanning rate of 20°/min, (a): between -85 and -30 °C; (b): between 35 and 150 °C.

Pure HHTPI curves exhibit a glass transition temperature of $-66\text{ }^{\circ}\text{C}$ and a strong relaxation phenomenon. When inserted in a polyurethane network, similar soft segment glass transition temperatures (T_{gs}) are obtained, displaying the highly microphased morphology of the polyurethane. For $r < 1$, T_{gs} increase is mainly affected by the molecular weight between crosslinks, \bar{M}_c , which decreases as hard segment content increases. For $r > 1$, T_{gs} is only affected by phase segregation. The slight increase observed indicates that HHTPI-based polyurethanes remain highly segregated. Similarly, increased hard segment glass transition temperatures observed for high isocyanate content (i.e. for $r > 1.3$) are attributed to the relaxation of organized isocyanurate structures within the hard segment. When observed, hard segment glass transition temperatures ($73\text{ }^{\circ}\text{C}$) were found to be close to the value for pure I-IPDI.

Soft segment glass transition temperatures (T_{gs}), ΔC_p of the soft phase, and the calculated segregation rate ξ according to Camberlin model, are listed in Table 1 for all prepared segmented materials.

ΔC_p values listed in Table 1 were calculated on a per gram of soft segment basis by taking into account only the quantity of HHTPI introduced in the formulation.

According to ξ values, clear microphase segregation is observed for HHTPI-based polyurethanes even when a large excess of isocyanurate is used. Microphase segregation for the stoichiometric reaction ($r=1.03$) led to a 81% soft segment segregation rate. A similar value was found by others for hydrogenated HTPB/MDI polyurethane systems (83%) [29]. An increase in crosslink density appears to increase phase mixing of the polyurethane linearly for $r > 1$, i.e. when a perfect network is obtained (Fig. 5). For $r < 1$, dangling chain content contributes to larger mobility, giving a higher microphase segregation and a ΔC_p value closer to that of pure polyol.

This is in agreement with other authors who observed better microphase segregation for linear polyurethane over the corresponding crosslinked ones, thus demonstrating the importance of chain mobility in this phenomenon [30,31].

Table 1
Soft segment glass transition temperature, specific heat capacity change at the glass transition, and soft-phase segregation rate of HHTPI/I-IPDI polyurethanes with different NCO/OH ratios and HHTPI starting polyol

NCO/OH	T_g ($^{\circ}\text{C}$)	ΔC_p ($\text{J g}^{-1} \text{K}^{-1}$)	ξ
HHTPI	-66.0	0.387	1
0.5	-64.7	0.384	0.99
0.6	-61.3	0.363	0.94
0.8	-59.2	0.340	0.88
1.03	-58.1	0.312	0.81
1.3	-57.4	0.294	0.76
1.7	-56.7	0.295	0.76
1.9	-57.5	0.283	0.73
2.2	-56.1	0.271	0.70

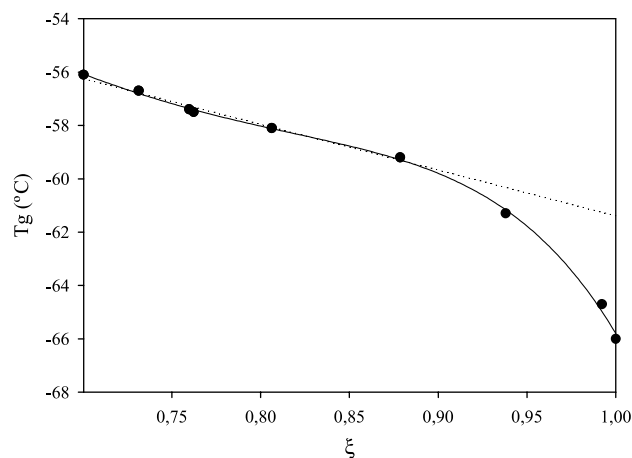


Fig. 5. Soft-phase segregation rate, ξ , versus soft segment glass transition.

3.3. Swelling measurements

The measured values of the polyurethane densities range between 0.91 and 0.99 g cm^{-3} (Table 2). Swelling behaviour of the polyurethanes having NCO/OH ratios from 0.5 to 2.2 were investigated in THF at room temperature. For $r < 1$, as more crosslinking agent is incorporated into the network structure, Q_s values decrease rapidly due to the crosslinking effect during network formation. For $r > 1$, the network is completed and additional crosslinking agent incorporation does not affect swelling measurements, as noted by the plateau (Fig. 6).

Swelling of networks is related to their elastic properties and enables crosslink density determination using the Flory–Rhener equation [32]:

$$\frac{\rho_p}{\bar{M}_c} = \nu_e = \frac{-[\ln(1 - \nu_2) + \nu_2 + \chi\nu_2^2]}{V_s(\nu_2^{1/3} - \frac{\nu_2}{2})} \quad (4)$$

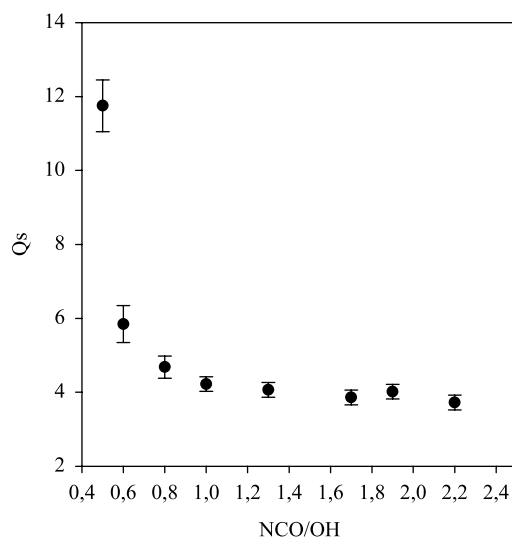


Fig. 6. Swelling measurements of polyurethanes in THF at room temperature versus NCO/OH ratio. Values are the mean of measurements. Error bars represent standard error of the mean.

Table 2

ρ_p , density of the polymer; ν_2 , volume fraction of the polyurethane in the swollen gel; ν_e , crosslink density; \bar{M}_c , values calculated from Flory–Rheener relationship

r	ρ_p (g cm ⁻³)	$1/Q_s$	ν_e	\bar{M}_c
0.5	0.91	0.0851	4.20×10^{-5}	21,680
0.6	0.91	0.1711	1.70×10^{-4}	5340
0.8	0.92	0.2136	2.76×10^{-4}	3330
1.03	0.94	0.2368	3.49×10^{-4}	2700
1.3	0.96	0.2458	3.80×10^{-4}	2530
1.7	0.97	0.2589	4.29×10^{-4}	2260
1.9	0.98	0.2489	3.91×10^{-4}	2500
2.2	0.99	0.2687	4.68×10^{-4}	2120

where \bar{M}_c is the molecular weight between crosslinks, ν_2 is the volume fraction of the polymer in the swollen gel, χ is the polymer–solvent interaction parameter, ρ_p is the density of polymer, and V_s is the specific volume of solvent, and ν_e is the crosslink density. If ν_2 is easily determined by swelling measurements (i.e. $\nu_2 = 1/Q_s$), χ may be obtained from the solubility parameter by the following equation:

$$\chi = \chi_S + \chi_H \approx 0.34 + \frac{V_s}{RT}(\delta_1 - \delta_2)^2 \quad (5)$$

where δ_1 and δ_2 are the respective solubility parameters of the solvent and polymer, and χ_S and χ_H are the entropic and enthalpic contributions. For THF, $\delta_1 = 19.14 \text{ J}^{1/2} \text{ cm}^{-3/2}$ and $V_s = 81.9 \text{ cm}^3 \text{ mol}^{-1}$ [33].

δ_2 of the polyol was first calculated using the group contribution method [34] and found to be 16.50, 16.94 and $17.0 \text{ J}^{1/2} \text{ cm}^{-3/2}$, according to Van Krevelen, Hoy and Small models, respectively. Swelling measurements using symmetric liquids, i.e. in which solubility parameters frame the predicted value, were used for a more accurate determination of δ_2 for the polyurethane network ($r=1$). Cyclohexane and acetone, whose respective solubility parameters are 16.70 and $19.77 \text{ J}^{1/2} \text{ cm}^{-3/2}$ [33], were selected. Swelling in such liquids is characterized by the presence of a maximum on the network swelling versus

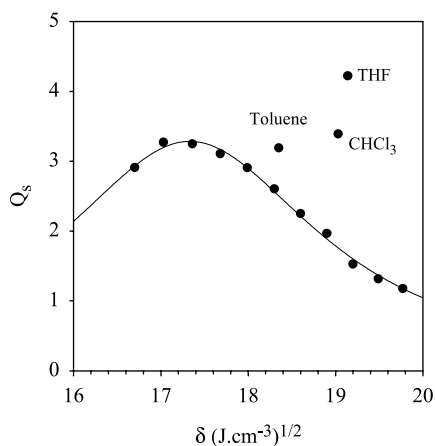


Fig. 7. Solubility parameter determination of HHTPI/I-IPDI PU ($r=1$) using symmetric liquids, cyclohexane $\delta = 16.70 \text{ (J cm}^3)^{1/2}$ and acetone $\delta = 19.77 \text{ (J cm}^3)^{1/2}$.

liquid phase solubility parameter curve. According to Fig. 7, δ_2 of the polyurethane network ($r=1$) was $17.2 \text{ J}^{1/2} \text{ cm}^{-3/2}$.

Equilibrium swelling value in THF, chloroform and toluene was also investigated because they well solubilize I-IPDI. The Q_s values were found to be higher than those obtained with the acetone/cyclohexane system (Fig. 7). This phenomenon was attributed to better solvation of the network and particularly of the urethane linkages. Oppositely we may assume that acetone/cyclohexane mixtures are good solvents of HHTPI but do not solvate properly the urethane groups. Thus THF being the solvent of the study we found more accurate to consider δ_2 of the network close to δ_1 of THF, which has the highest equilibrium swelling value. Assuming $\delta_1 \approx \delta_2$, $\chi = 0.34$ was determined according to Eq. (5).

From Eq. (4), ν_e and \bar{M}_c were calculated for the different NCO/OH ratios and summarized in Table 2. As expected, crosslink density increased as the NCO/OH ratio increased, whereas \bar{M}_c , which is inversely proportional to crosslink density, decreased (Fig. 8).

A relationship between T_g and \bar{M}_c was obtained by Fox and Loshaek [36]. Andradý et al. [35] modified this relationship by studying the dependence of T_g on polyurethane network structures based on poly (oxypropylene) crosslinked by a triisocyanate. By replacing T_g^∞ ,

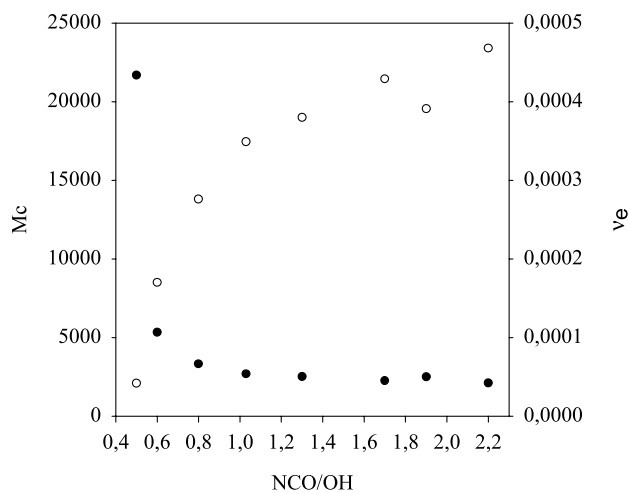


Fig. 8. (O): crosslink density, ν_e , and (●): molecular weight between crosslink, \bar{M}_c , versus NCO/OH ratio.

corresponding to the T_g of a linear polymer of infinite molar mass in the Fox and Loshaek equation, by the T_{gs}^0 of the oligomer, the shift that occurs when blocking chain ends to form the network is taken into account (Eq. (7)).

$$T_{gs} = T_{gs}^0 + \frac{K}{\bar{M}_c} \quad (7)$$

The plot of T_g versus $1000/\bar{M}_c$ (Fig. 9) shows that T_g of the studied PU networks varies linearly with $1000/\bar{M}_c$ over the studied range ($0.5 > r > 2.2$) and leads to $K = 2.0 \times 10^4 \text{ K mol g}^{-1}$. The ordinate at the origin value ($-65.3 \text{ }^\circ\text{C}$), close to the polyol glass transition temperature ($-66 \text{ }^\circ\text{C}$), suggests that the elastically active network chains were only composed of HHTPI.

The calculated value of K ($2.0 \times 10^4 \text{ K mol g}^{-1}$) is close, to values obtained by Bengtson et al. [37] ($5.7 \times 10^4 \text{ K mol g}^{-1}$) for a HTPB/TDI system, Nabeth et al. [38] ($6.1 \times 10^4 \text{ K mol g}^{-1}$) for PU networks based on hydroxyl terminated polycaprolactone/trimethylol propane/tetramethylxylene diisocyanate and, Andrady et al. constant value ($2.5 \times 10^4 \text{ K mol g}^{-1}$) for a model polyurethane system. According to Nabeth et al. [38] and Rietsch et al. [39], values of K are linked to the average functionality of the crosslinks and reflect the intermolecular interactions near the crosslink points. For the synthesized polyurethane materials I-IPDI is used. This isocyanurate has an average functionality of 3.43 [14] which can be considered as the average functionality of the crosslinks. However the resulting K value is lower than the reported ones for diisocyanate-based materials [37,38] suggesting that fewer intermolecular interactions are present near the crosslink points compared to the cited systems.

4. Conclusion

Properties of new polyurethanes were assessed by means of rheological, swelling and DSC analyses. In spite of some

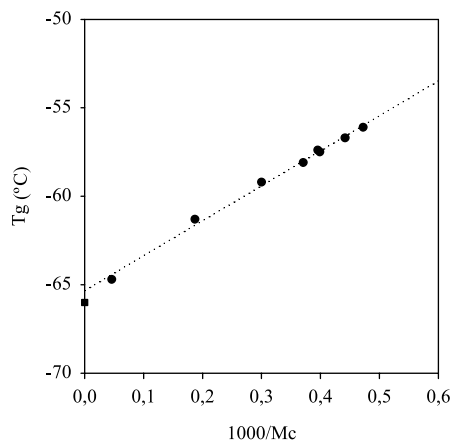


Fig. 9. Glass transition temperature dependence on polyurethane network structure, T_g versus $1000/\bar{M}_c$. v : T_g of HHTPI.

approximations, the critical gel point estimated by Macosko Miller model is close to the one obtained by rheological measurement using Winter model. DSC and swelling measurements highlighted the microphase segregation of the synthesized polyurethanes. It was observed that phase mixing and T_{gs} slightly increased when hard segment content increased. As commonly observed in polyurethanes, the elastically active network chains were mainly composed of the polyol, i.e. HHTPI in our case.

References

- [1] Oertel G. Polyurethane handbook. 2nd ed. Munchen: Hanser; 1994.
- [2] Yee RY, Adicoff AJ. J Appl Polym Sci 1976;20:1117.
- [3] Brunette CM, Hsu SL, MacKnight WJ. Polym Eng Sci 1981;21:163.
- [4] Iwama A, Hasue K, Takahashi T, Matsui K, Ishiura K. Propellants, Explosives, Pyrotechnics 1996;21:43.
- [5] Camberlin Y, Gole J, Pascault JP. Angew Makromol Chem 1981;95:67.
- [6] Byrne CA, McHugh EA. Polym Preprints 1990;31:657.
- [7] Flandrin FR, Widmaier JM, Flat JJ. Polym Degrad Stab 1997;57:59.
- [8] Flandrin FR, Flat JJ, Widmaier JM. UTECH'96 The Hague (Nederland). Conference Proceedings 1996. Paper 45.
- [9] Burel F, Feldman A, Bunel C. Polymer, in press.
- [10] Macosko CW, Miller DR. Macromolecules 1976;9:199.
- [11] Miller DR, Macosko CW. Macromolecules 1976;9:206.
- [12] Burel F, Oulyadi H, Bunel C. Int J Polym Anal Charact 2000;6:193.
- [13] Burel F, Feldman A, Bunel C, Oulyadi H. J Pol Anal Charact 2003;8:301.
- [14] Burel F, Feldman A, Bunel C. e-polymer 2004;011.
- [15] Djabourov M, Leblond J, Papon P. J Phys Fr 1988;49:333.
- [16] Tung CM, Dynes J. J Appl Polym Sci 1982;27:569.
- [17] Winter HH, Chambon F. J Rheol 1986;30:367.
- [18] Winter HH, Chambon F. J Rheol 1987;31:683.
- [19] Muller R, Gerard E, Dugand P, Rempp P, Gnanou Y. Macromolecules 1991;24:1321.
- [20] Yu JM, Jerome R, Teyssie P. Polymer 1997;38:347.
- [21] Chambon F, Petrovic Z, Macknight WJ, Winter HH. Macromolecules 1986;19:2146.
- [22] Winter HH, Morganelli P, Chambon F. Macromolecules 1988;21:532.
- [23] Brunette CM, Hsu SL, Macknight WJ, Schneider NS. Polym Eng Sci 1981;21:163.
- [24] Camberlin Y, Pascault JP. J Polym Sci—Polym Chem Ed 1982;20:1445.
- [25] Bengston B, Feger C, Macknight WJ, Schneider NS. Polymer 1985; 26:895.
- [26] Xu M, Macknight WJ, Chen CHY, Thomas EL. Polymer 1983;24: 1327.
- [27] Chen CHY, Briber RM, Thomas EL, Xu M, Macknight WJ. Polymer 1983;24:1337.
- [28] Brunette CM, Hsu SL, Rossman M, Macknight WJ, Schneider NS. Polym Eng Sci 1981;21:668.
- [29] Camberlin Y, Pascault JP. J Polym Sci—Polym Chem Ed 1983;21: 415.
- [30] Thomas O, Priester RD, Hinze KJ, Latham DD. J Polym Sci Polym Phys 1994;32:2155.
- [31] Li Z, Yang G, Xu C. J Polym Sci Polym Chem 2004;42:1126.
- [32] Flory PJ, Rhener JJ. J Chem Phys 1943;11:521.
- [33] Yaws CL. Chemical properties handbook. New York: McGraw-Hill; 1999.
- [34] Van Krevelen DW. Properties of polymer. Amsterdam: Elsevier; 1990.
- [35] Andrady A, Sefcik D. J Polym Sci Polym Phys 1983;21:2453.
- [36] Fox TG, Loshaek S. J Polym Sci 1955;15:371.
- [37] Bengston B, Feger C, Macknight WJ, Schneider NS. Polymer 1985;26:895.
- [38] Nabeth B, Pascault JP, Dusek K. J Polym Sci, Polym Phys 1996;34: 1031.
- [39] Rietsch F, Daveloose D, Froelich D. Polymer 1976;7:859.