The Effect of Crosslinking on Properties of Polyurethane Elastomers

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SYNOPSIS

A series of segmented polyurethanes from two polyols, 4,4'-diphenylmethane diisocyanate (MDI) and butane diol was synthesized. The degree of chemical crosslinking was controlled by varying the ratio of poly(oxypropylene)diol to poly(oxypropylene/oxyethylene)triol. The samples were prepared at the stoichiometric ratio of NCO to OH groups and at a constant concentration of hard segments (butane diol; MDI) equal 50 wt %. At low concentrations of the triol the molecular weight of the polyurethanes increases; at higher concentrations (above 9 mol %) crosslinked products are obtained. All samples show a distinct two-phase structure and in the region of 0–150°C the dynamic mechanical behavior is affected by the hard phase. Chemical crosslinking was found to increase the tensile strength and strain at break, but did not affect appreciably the tear strength, hardness, and soft segment glass transition. The stress relaxation rate at room temperature was found to depend both on the elongation and on the degree of crosslinking. A comparison of the sol fractions w_s found for crosslinked samples with the predictions of the theory of branching processes proved that the achieved conversions of reactive groups in networks are high (~ 0.98).

INTRODUCTION

Segmented polyurethanes exhibit networks behavior at room temperature, where the role of the crosslinks is played by the hard domains. Strained samples tend to relax considerably, especially at elevated temperatures. Introduction of chemical crosslinks is expected to modify the overall behavior of these polymers. Chemical crosslinking can be introduced either in the hard segment using a short polyol (functionality $f > 2$) as the chain extender or in the soft segment using long triols or higher functionality polyols with or without long diols. The short triols used as chain extenders, such as trimethylolpropane (TMP), combined with 4,4'-diphenylmethane diisocyanate (MDI), lower the crystallinity of the hard segment in comparison with linear diols and yield lower strength elastomers. Yokoyama[1] found that TMP with hexamethylene diisocyanate and a poly(oxyethylene)diol (PEO) gave polyurethane elastomers with mechanical behavior typical of amorphous polymers. Unlike diamine extended polyurethanes, they did not exhibit Mullins effect during stretching. However, if crosslinks are introduced via combination of linear and tri- or multifunctional polyols, the effect is different. At temperatures where hard segments are operative (below their melting points), the effect of chemical crosslinking is expected to be superimposed on the effect of physical crosslinking. Above the melting point of the hard segments and also in solution only chemical crosslinks are operative. The effect of peroxide crosslinking of thermoplastic urethanes was described by Schollenberger and Dinbergs.[2] They found that random crosslinking of the thermoplastic polyesterurethane decreased slightly the tear strength, slowed down the stress–relaxation rate, and improved solvent resistance.

In this work, chemical crosslinking in segmented polyurethanes was introduced via a long triol, and the effect of combined chemical and physical crosslinking on their properties was examined. Soft segment concentration (SSC) was kept constant at 50 wt % and so was the structure of the hard segment (MDI/butane diol). Soft segment length was controlled by the length of the poly(oxypropylene)diol having nominal molecular weight M_n of 2000 and the poly(oxypropylene/oxyethylene) triol having nominal M_n of 3500. If a trifunctional component is added in a mixture of difunctional compounds at the stoichiometric ratio of reacting groups, gelation of the system occurs at a conversion which depends on the amount of trifunctional material. Gelation, sol fraction, the degree of swelling, and mechanical properties of the chemically and physically crosslinked networks were measured as a function of the triol concentration.

EXPERIMENTAL

Materials

Polyurethane elastomers based on 4,4'-diphenylmethane diisocyanate (MDI), butane diol, and two polyols were prepared. The polyols used were: poly(oxypropylene)diol (PPO) produced by Soda-So (Tuzla, Yugoslavia) under commercial name Salinol 2501, having M_n = 1908 (OH number = 58.8 mg KOH/g, water content 0.02 wt %, and acidity 0.018%), and block copolymer of poly(oxypropylene/oxyethylene) endcapped triol (PPO/PEO), having M_n = 3499 (content of ethyleneoxide 15 wt %, OH number = 48.1 mg KOH/g, content of H_2O

= 0.03 wt %, and acidity = 0.021%) under commercial name Salinol TPE 3501. The degree of crosslinking was varied by varying the ratio of the diol to the triol. Table I displays all nine diol/triol combinations. Butane diol was distilled prior to synthesis. Commercial 4,4'-diphenylmethane diisocyanate (MDI), Suprasec MPR from ICI (U.K.) was used as received. The insoluble part was removed by decanting. Dibutyltin dilaurate (~ 0.001 wt %) (DBTDL) was used as the catalyst.

Preparation of Samples and Methods of Measurements

The concentration of the soft segment was always kept constant at 50 wt %. The synthesis was carried out by prepolymer technique. The polyol and diisocyanate were mixed and heated at 60–70°C for 1 h under dry nitrogen. Then, butane diol chain extender and DBTDL catalyst were added. After mixing for about 15 s the mixture was poured into a heated mold, kept under pressure at 100°C for about 20 min, and subsequently taken out of the mold for post-curing at 80°C for 24 h. The elastomers were allowed to equilibrate for at least 7 days before testing.

Stress–strain properties were measured on the Instron tensile tester, Model 1185. Tensile strength σ_b and strain at break, ϵ_b, were measured according to ASTM D 412-68 and tear strength R according to ASTM D 624. Tensile experiments were performed on samples 30 mm in length at an extension rate of 50 mm/min. Stress–relaxations were measured at 50, 100, and 150% elongations and the dependences of Young modulus $E(t)$ were determined at room temperature. DSC measurements were carried out on the DuPont DSC, Model 910. Dynamic

Table I   Designation, Composition and Some Properties of the Polyurethanes[a]

Sample No.	d (g/cm³)	Wt % of Diol	Mole Fraction of the Triol	w_g	v_2	$[\eta]$ (dL/g)
1	1.05	100	0	—	—	0.30
2	1.10	97	0.0166	—	—	0.31
3	1.12	94	0.0336	—	—	0.54
4	1.12	90	0.0571	—	—	0.56
5	1.15	85	0.0878	—	—	0.57
6	1.15	80	0.12	0.138	0.00456	—
7	1.15	60	0.2667	0.471	0.02562	—
8	1.15	30	0.56	0.864	0.09651	—
9	1.11	0	1	0.968	0.17153	—

[a] d is the density, w_g is the weight fraction of the gel, v_2 is the volume fraction of the polymer in swollen state, and $[\eta]$ is the intrinsic viscosity.
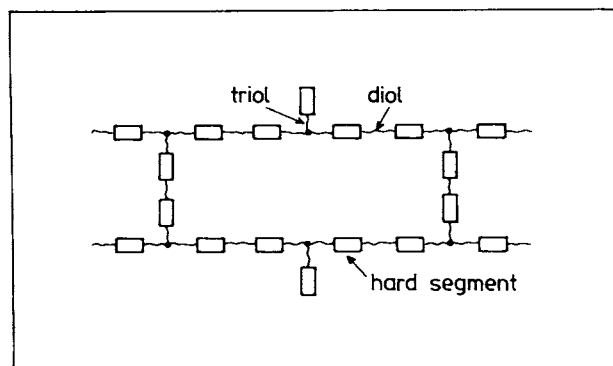
Figure 1 Schematic representation of the network structure.

mechanical behavior was measured in the temperature range 100–200°C on the Rheometrics System IV apparatus at a constant frequency $\omega = 1$ Hz; both components of the complex shear modulus $G^*(\omega)$ $(= G' + G''$, where G' and G'' are the storage and loss modulus, respectively) were determined. Hardness was determined on the Shore A hardness tester according to ASTM D 2240-68. Intrinsic viscosities $[\eta]$ of soluble samples were measured in dimethylformamide (DMF) at 25°C.

Extraction and swelling measurements were carried out at room temperature in DMF. The weight fraction of the gel, w_g, and the volume fraction of the polymer in the swollen sample, v_2, were also determined (Table I).

RESULTS AND DISCUSSION

The structure of networks is shown in Figure 1. For the theoretical description of the network formation,

the theory of branching processes were used (cf. Appendix). The changes of the weight fraction of the gel, w_g, and concentration of elastically active network chains (EANC), ν_e (or its reciprocal value, $M_c = d/\nu_e$, d is the density of sample) were calculated depending on conversion of OH groups, ξ_B, in the second stage of reaction. Also, the critical conversion, ξ_{Bg}, at the gel point was calculated. In Table II, the values for full conversion $\xi_B = 1$, $\nu_e^{(1)}$, and $M_c^{(1)}$ are given; for samples 6–9 also the values $\nu_e^{(2)}$ and $M_c^{(2)}$ were calculated for conversion ξ_{Bx}, which corresponds to the experimental sol fractions w_g.

The results in Table II indicate that practically full conversion of groups would be necessary for a network structure to be formed. The fact that these samples are soluble gives evidence that full conversion has not been reached. Also, for samples 6–9 with a higher fraction of triol the conversions ξ_{Bg} are relatively high. The existence of a network structure in these samples proves that the conversions are indeed high; the values of ξ_{Bg} calculated from w_g are 0.975–0.985. The concentrations of EANCs $\nu_e^{(2)}$ are considerably smaller than $\nu_e^{(1)}$. Thus, the crosslinking density is strongly affected by the extent of the reaction.

From the values of $\nu_e^{(2)}$ and the volume fraction of the polymer in the network swollen to equilibrium v_2 in DMF, the Flory–Huggins interaction parameter χ was calculated using the relation

$$\chi = -[\nu_e^{(2)}V_1(v_2^{1/3} - 2v_2/3)$$
$$+ \ln(1 - v_2) - v_2]/v_2^2 \quad (1)$$

where V_1 is the molar volume of the solvent ($= 76.78$

Table II Structural Parameters of the Networks[a]

Sample No.	ξ_{Bg}	$\xi_{Bx}\ (w_g)$	$\nu_e^{(1)}\ (\xi_B = 1)$	$\nu_e^{(2)}\ (\xi_B)$	$M_c^{(1)}\ (\xi_B = 1)$	$M_c^{(2)}\ (\xi_B)$
1	1	—	—	—	—	—
2	0.9975	—	7.01×10^{-6}	—	155,000	—
3	0.995	—	1.43×10^{-5}	—	78,000	—
4	0.992	—	2.39×10^{-5}	—	46,500	—
5	0.987	—	3.70×10^{-5}	—	31,000	—
6	0.984	0.985	4.91×10^{-5}	2.57×10^{-7}	23,400	3,800,000
7	0.968	0.976	9.85×10^{-5}	3.52×10^{-6}	11,670	327,000
8	0.947	0.976	1.73×10^{-4}	3.72×10^{-5}	6650	30,900
9	0.927	0.979	2.36×10^{-4}	9.37×10^{-5}	4660	11,850

[a] ξ is the conversion, ν_e is the concentration of elastically active network chains (EANCs), and $M_c = d/\nu$ is the number-average molecular weight of EANC.
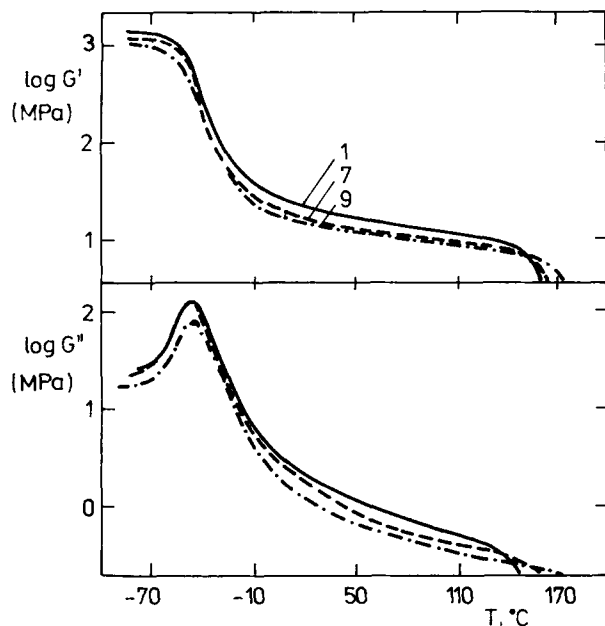
Figure 2 Temperature dependences of the storage (G') and loss (G'') moduli measured at $\omega = 1$ Hz. Numbers at curves correspond to samples in Table I.

Physical and Mechanical Properties of Elastomers

The dynamic mechanical behavior corresponds to a distinct two-phase structure of elastomers (Fig. 2). The position of the main transition for the soft component on the temperature scale ($T_m \approx -50°C$) is not affected by the content of triol and correlates well with T_g. Also, the modulus G' does not depend on composition in the region of 0–150°C, which gives evidence of the decisive effect of the hard phase on G'. For example, the experimental value $G' \approx 20$ MPa (samples 9) at $\sim 20°C$ is higher by a factor of 80 than G' coming from the contribution by the covalent crosslinks alone ($G' \sim \nu_e^{(2)}RT$). Similar behavior was found also in other segmented polyurethane systems.[3,4] Melting takes place in all samples above 170°C.

Hardness (~ 90 Shore A) did not vary with the concentration of the crosslinker. Hardness is primarily governed by the hard segment concentration, which was in all cases 50 wt %. Tensile strength σ_b was found to increase continuously with increasing crosslinking up to 56 mol % of the crosslinker and then remains constant (Fig. 3). According to Smith,[5,6] the strength of elastomers is related to the relaxation time of mobile chains. Microcrack propagation depends on chains mobility. Smith also found that hard segments in segmented polyurethanes were highly effective sources of strength, impending crack growth. Taking into account that the physical structure is more or less the same in all polymers, it appears that crosslinks slow down chain
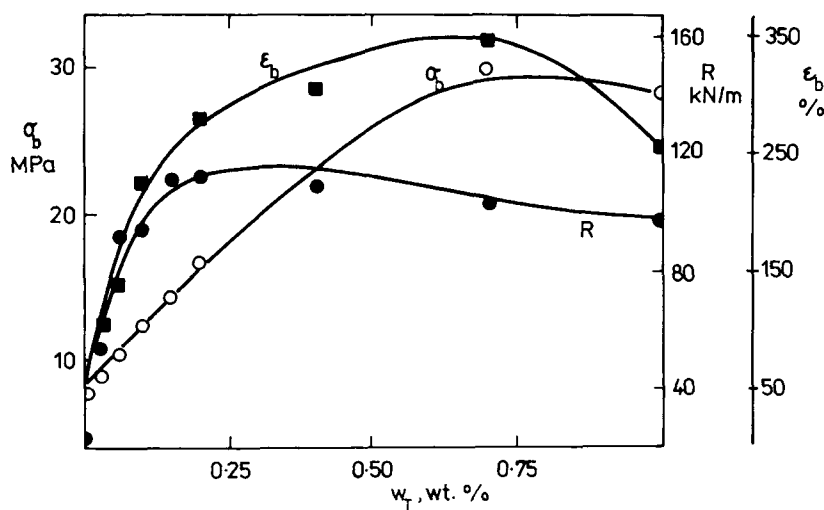
mL/mol). For samples 6–9, the following values of the interaction parameter χ were found: 0.361, 0.395, 0.414, and 0.457. The increase of χ with increasing triol concentration may be caused by increasing concentration of the polymer and possibly also by increasing concentration of oxyethylene units in the samples.

Figure 3 The effect of triol concentration on the tensile strength σ_b, strain at break ϵ_b, and tear strength R.
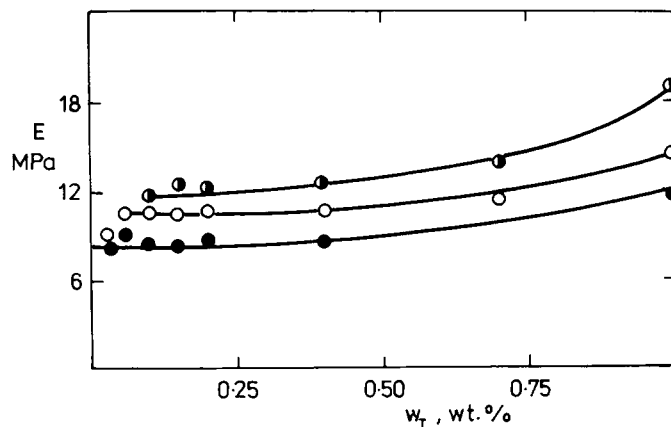
Figure 4 Dependence of Young modulus E measured at $t = 100$ s on the triol concentration. Elongations: (●) 50%; (○) 100%, (◑) 150%.

relaxations during extension. Strain at break, ϵ_b, was found to have a maximum at 56 mol % of triol (Fig. 3). It usually decreases with the increase of the crosslinking density.[5] That is true, however, in densely crosslinked elastomers, which is not the case here.

Tear strength R increases with the crosslinking density up to 12 mol % of the triol. Further increase of crosslinker content caused a mild decrease in tear

strength (Fig. 3). It could be concluded that once the network is formed, the tear strength is practically independent of the crosslinking density.

The dependence of the Young modulus E on the crosslinker concentration at 50, 100, and 150% extension is given in Figure 4. The effect of crosslinking is evident only above 27 mol % of triol, being more pronounced at higher extensions. When triol alone was used as the soft segment, the 150% mod-
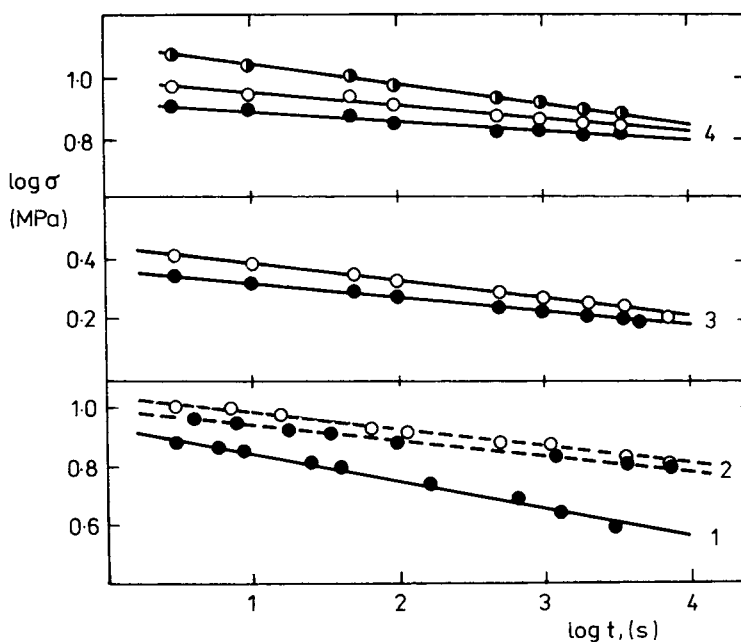

Figure 5 An example of the relaxation curves at different elongations. Numbers at curves correspond to samples in Table I. Elongations: (●) 50%; (○) 100%; (◑) 150%.
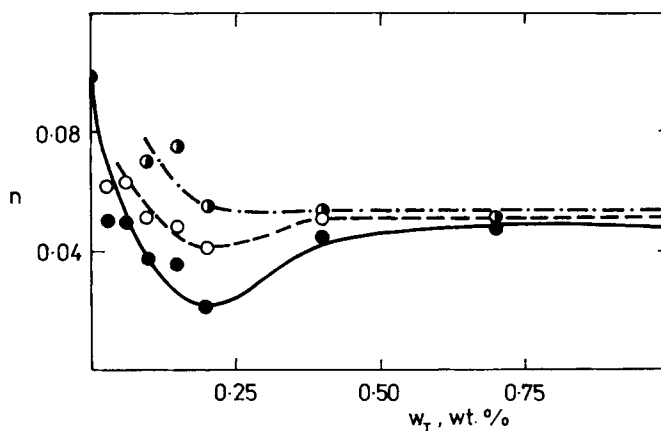
Figure 6 The effect of triol concentration on the relaxation rate n. Elongations: (●) 50%; (○) 100%; (◑) 150%.

ulus was higher by about 50% than that of the uncrosslinked elastomer. This could be interpreted as the effect of slower relaxation in the former.

Stress relaxations were measured at 50, 100, and 150% elongations where possible. Figure 5 shows log σ — log t plots over about four decades of time on several samples. Other relaxation curves follow the same pattern. The dependences are described by straight lines. Relaxation rates $n = -d \log \sigma / d \log t$, which are the slopes of the curves were calculated by linear regression. Figure 6 shows the effect of the crosslinker concentration on the relaxation rate. It appears that n increases with extension and decreases with increasing triol content up to 12 mol % of the triol. Above this concentration n increases to a constant value up to 100% of triol. At 150% extension the picture is somewhat different. Relaxation rate at low triol contents decreases with the increase of the triol up to 12 mol % to a constant value. It is interesting to mention that at 12 mol % of triol an insoluble network was formed. One can assume that relaxation rate is primarily determined by the size of the hard domains. At 50% SSC, the morphology of segmented polyurethanes is characterized by bicontinuous phases and an interlocking structure has been proposed.[7] The stress–strain curves of these polyurethanes showed no distinct yield point characteristic of breaking of hard segments.

CONCLUSIONS

A study of crosslinking of segmented polyurethanes has shown that the polymers are soluble in DMF below 12 mol % of the triol. A higher content of triol caused gelation and network formation. Crosslinking affected neither the glass transition of the soft segment nor the melting point of the hard segment domains. Tensile strength and strain at break increased with increasing degree of crosslinking up to 56 mol % of the triol and the tear strength up to 12 mol % of the triol. The stress–relaxation rate was found to depend on both extension and the degree of crosslinking.

APPENDIX: CALCULATION OF STRUCTURAL PARAMETERS OF NETWORKS

The networks were prepared in two stages. In all experiments, a large excess of isocyanate groups was used in the first stage ($[NCO]_0/[OH] \cong 7$). Consequently, the content of oligomers (containing more than one polyol unit) was negligible (the fraction of diisocyanate units reacted with both isocyanate groups was $\sim 2\%$). Therefore, the system can be considered as consisting of three components terminated by isocyanate groups (A):

NCO endcapped PPO/PEO triol	TA	n_{TA}
NCO endcapped PP diol	DA	n_{DA}
diisocyanate–MDI	MA	n_{MA}

where n is the molar mole fraction of the respective component.

The other component is butandiol B having two OH groups (B) and its mole fraction is n_B.

In analogy with the approach used in Ref. 8, one can formulate the probability generating functions (pgf's) for the number of bonds issuing from units terminated by A

and B groups, respectively, in the system (i.e., in the root) as follows:

$$F_0(z_B) = [n_{TA}(1 - \xi_A + \xi_A z_B)^3 + (n_{DA}$$
$$+ n_{MA})(1 - \xi_A + \xi_A z_B)^2]/n_A \quad (2)$$

$$F_0(z_A) = (1 - \xi_B + \xi_B z_A)^2 \quad (3)$$

where ξ_A and ξ_B are conversions of groups A (NCO) and B (OH), respectively, and

$$n_A = n_{TA} + n_{DA} + n_{MA}$$
$$n_A + n_B = 1$$

The pgf's for the number of bonds issuing from a unit in generation g to units in generation $g + 1$ ($g > 0$) is obtained by differentiation of pgf's (2) and (3) and renormalization

$$F_A(z_B) = \Phi_{TA}(1 - \xi_A + \xi_A z_B)^2$$
$$+ (\Phi_{DA} + \Phi_{MA})(1 - \xi_A + \xi_A z_B) \quad (4)$$

$$F_B(z_A) = (1 - \xi_B + \xi_B z_A) \quad (5)$$

where Φ are fractions of A groups in the components:

$$\Phi_{TA} = 3n_{TA}/S, \quad \Phi_{DA} = 2n_{DA}/S, \quad \Phi_{MA} = 2n_{MA}/S$$
$$S = 3n_{TA} + 2n_{DA} + 2n_{MA}$$

The critical conversion at the gel point (subscript g) is a function of derivatives of F_A and F_B and is given by the following expression:

$$(\Phi_{MA} + \Phi_{DA} + 2\Phi_{TA})\xi_{Ag}\xi_{Bg} = 1 \quad (6)$$

or

$$\xi_{Ag} = [r(\Phi_{NA} + \Phi_{DA} + 2\Phi_{TA})]^{-1/2} \quad (7)$$

where $r = [A]_0/[B]_0$ is the initial molar ratio of the reactive groups.

The probabilities that a bond has a finite continuation (extinction probabilities) are determined by the recursive equations

$$v_A = F_A(v_B) \quad \text{and} \quad v_B = F_B(v_A) \quad (8)$$

After substitution from eqs. (4) and (5) and elimination of the trivial roots $v_A = v_B = 1$, one gets

$$1 - v_B = [\xi_A\xi_B(2\Phi_{TA} + \Phi_{DA} + \Phi_{MA}) - 1]/\xi_B\xi_A^2 \quad (9)$$

$$1 - v_A = (1 - v_B)\xi_B \quad (10)$$

The sol is composed of units which issue bonds with finite continuation only; therefore, the probability that a

bond is formed (ξ) is weighted by the probability that it is finite (v):

$$w_s = m_{TA}(1 - \xi_A + \xi_A v_B)^3 + (m_{DA} + m_{MA})$$
$$\times (1 - \xi_A + \xi_A v_B)^2 + m_B(1 - \xi_B + \xi_B v_A)^2 \quad (11)$$

where m are weight fraction of components; e.g.,

$$m_{TA} = n_{TA} M_{TA}/M$$

where

$$M = n_{TA}M_{TA} + n_{DA}M_{DA} + n_{MA}M_{MA} + n_B M_B$$

is the average molecular weight of the components.

The number of elastically active network chains (EANCs), N_e, is determined by the number of bonds with infinite continuation issuing from active branch points, i.e., from units with three and more bonds with infinite continuation. The distribution of active branch points with respect to the number of bonds with infinite continuation can be obtained from F_{0A} and F_{0B}. Here, however, it is only the PPO/PEO triol unit which can contribute to the number of EANCs. In that case, all three bonds must have infinite continuation. Therefore,

$$N_e = (3/2)n_{TA}\xi_A^3(1 - v_B)^3 \quad (12)$$

The concentration of EANCs per unit volume of the gel reads

$$v_e = N_e/M(1 - w)_s \quad (13)$$

where d is the density of the gel.

The structural parameters were calculated from the initial composition which can be determined either by the mole fractions of the PPO/PEO triol, n_{TO}, PP diol, n_{DO}, and MDO, n_{MO}, and butane diol, n_B, or by the fraction of groups in these components.

For calculation of the network parameters, we need the fractions of species after the first stage characterized by mole fractions n_{TA}, n_{DA}, n_{MA}, and n_B. The relations follow from materials balance. If we designate the number of moles of the respective components by N, then

$$N'_{TA} = N_{TO}$$
$$N_{DA} = N_{DO}$$
$$N_{MA} = N_{MO} - 3N_{TO} - 2N_{DO}$$

because each OH group reacts with an MDI molecule.

Using these relations, one gets

$$n_{TA} = N_{TA}/(N_{TA} + N_{DA} + N_{MA} + N_B)$$
$$= N_{TO}/(N_{MO} - 2N_{TO} - N_{DO} + N_B)$$
$$= n_{TO}/(n_{MO} - 2n_{TO} - n_{DO} + n_{BO})$$

$$n_{DA} = n_{DO} / (n_{MO} - 2n_{TO} - n_{DO} - n_{BO})$$

$$n_{MA} = (n_{MO} - 3n_{TO} - 2n_{DO}) / (n_{MO} - 2n_{TO} - n_{DO} + n_{BO})$$

From the mole fractions, the fractions of groups Φ can be calculated as shown above.

The number-average molecular weights of components are as follows:

$$M_{TA} = 4250, \quad M_{DA} = 2400, \quad M_{MA} = 250,$$

$$\text{and} \quad M_B = 90$$

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