lecular motions. The strengths of the dielectric glass–rubber relaxation of *cis*-PCDO and the cis/trans copolymers are rather small in comparison with those corresponding to the cis and trans isomers of poly(1,4-cyclohexanedimethanol sebacate),[8] in spite of the fact that dielectric experiments were performed on totally amorphous polymers in the former case and in partially crystalline polymers in the latter. This may be due in part to the difference in polarity between cycloaliphatic polyformals and cycloaliphatic polyesters. In general, gauche states about CH_2–O acetal bonds in the CH_2O–CH_2–OCH_2 sequences of PCDO chains have an energy ca. 1.2 kcal mol^{-1} below that of the alternative trans states. Consequently, there is a high fraction of $g^{\pm}g^{\pm}$ conformations about two consecutive acetal bonds, and here the dipoles associated with the CH_2OCH_2 groups are placed in an almost antiparallel direction. These conformations do not contribute to the dipole moment of the chains, and hence the low polarity of PCDO networks, independently of the cis/trans content. Actually, the dipole moment of these polymers, expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ ($\langle\mu^2\rangle$ is the mean-square dipole moment of the chains and nm^2 the value of this quantity for a freely jointed chain of similar number of skeletal bonds) is only[20] 0.167. This value contrasts with the values of 0.983 and 0.631 found for the cis and trans isomers of poly(1,4-cyclohexanedimethanol sebacate),[21] respectively.

Concluding Remarks

The results discussed above seem to suggest that the β relaxations in PCDO networks, both cis and cis/trans, are produced by complex molecular motions involving more than a single structural unit. The fact that the activation energy for the mechanical and dielectric relaxations is similar in both cases and its value is significantly larger than 11.5 kcal mol^{-1}, the energy involved in the chair-to-chair inversion, strongly supports the assumption that conformational changes in the skeletal bonds of the acyclic part of the chains, rather than cyclohexylene flipping motions, are the cause of the relaxation.

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Registry No. *cis*-PCDO, 117942-62-8; *trans*-PCDO, 117942-63-9.

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In Situ Sequential Polyurethane/Poly(methyl methacrylate) Interpenetrating Polymer Networks: Structure and Elasticity of Polyurethane Networks

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ABSTRACT: As part of a study concerning polyurethane/poly(methyl methacrylate) interpenetrating polymer networks (IPNs), polyurethane networks were synthesized at various dilutions of the reaction medium and at different values of the NCO/OH ratio. The network defects arising in such materials were evaluated by three independent experimental approaches: solvent extraction, swelling behavior, and elastic modulus. It was found that networks with the least defects are formed at high precursor concentration, with a NCO over OH excess of about 7%. Different theories leading to the structural parameters of polymer networks were utilized and corroborate well with the experimental results. The study provides a means of classification of these polyurethane networks according to the amount of their defects; furthermore, it allows one to investigate the influence of the network formed first on the formation of the second network in sequential IPNs, and consequently on the ultimate properties of the material.

Introduction

Polymers may be combined in different ways, but due to their mutual incompability, they tend to a more or less pronounced phase separation. From an industrial point of view, interpenetrating polymer networks (IPNs),[1–4] in which the polymers coexist in the form of their physically entangled networks, are very interesting materials. However, such combinations are quite complicated to study, and only few of the usual investigation methods are suitable for the study of IPNs. This explains why general structure–properties relationships have not yet been established. Only their synthesis and some application-oriented properties are usually described in the literature. Also, the chemical aspects of the formation of an IPN, like the kinetics, the viscosity, the compability changes, ..., have rarely been reported.

Table I
Characterization of the Pluriisocyanate L75[a]

M_n	w_i, %	n_i, %	f_i
460	19	30	2
660	43	50	3
1280	23	14	4
1740	15	6	5

[a] M_n, number-average molecular weight determined by GPC; w_i, weight fraction; n_i, mol fraction; f_i, functionality.

Among the different systems under investigation in this laboratory,[5-7] IPNs based on an elastomeric polyurethane combined with a rigid methacrylic phase have been studied from a chemical point of view. After having examined how one network is formed in the presence of the other or of its precursors, and their respective kinetics,[8,9] we report a specific study of the polyurethane network which is formed first in the present preparation method and acts therefore as the host network toward the methacrylic component. The aim is to characterize the networks and thus to know more precisely the actual medium in which the second network is formed.

The first part of this study is devoted to the analysis of the sol fraction and to the determination of the swelling degree and of the compression modulus of various polyurethane networks. In the second part, these results have been utilized in several theoretical models describing the elastic behavior of polymer networks. The purpose was to corroborate the experimental conclusions and to classify our networks among themselves. Thus, the number of elastically active chains and the number of cross-linking sites have been determined after adaptation of the Miller–Macosko theory[10,11] to our system. The elastic behavior of the various polyurethane samples has been compared to that of the affine[12] and "phantom"[13] networks. Finally, de Gennes' scaling law concept[14] has also been applied to the system.

Experimental Part

Materials. Isocyanate (L75). Desmodur L75, provided by Bayer AG, is a 1,1,1-trimethylolpropane/toluene diisocyanate (TMP/TDI) adduct containing 25% ethyl acetate by weight. Density, 1.17 g/mL; NCO equivalent weight per kilogram, 3.06 (by standard titration with *n*-butylamine). L75 was used as received. If L75 is kept in dry and cool atmosphere, its isocyanate content does not change over at least 6 months, in spite of frequent sampling. Gel permeation chromatography (GPC) has shown that L75 contains in fact four species of different molecular weights and functionalities (Figure 1 and Table I). In principle, only TMP/TDI associations can be formed, so that the second peak (M_n = 660 g/mol) has been attributed to the triisocyanate (see Scheme I), where one molecule of TMP has reacted with three molecules of TDI. The higher molecular weight derivatives may result from complete reactions of TDI; i.e., each NCO group is linked to one TMP, the remaining four hydroxyl groups having reacted each with one TDI. By involving one more TMP, the 3:7 TMP/TDI derivative is formed, with a functionality of 5. The calculated molecular weights are 1138 and 1620 g/mol, respectively, and compare well with the experimental value found by GPC. The chemical nature of the peak with the lowest M_n has not been determined, but a combination of TDI and TMP is not possible as no remaining hydroxyl group was found by infrared analysis of L75. Its functionality has been calculated from the total NCO content and from that of the three above postulated TMP/TDI adducts. A value close to 2 has been found. Some residual TDI (less than 1 wt %) was also found by analysis.

Poly(oxypropylene glycol) (POPG). The POPG used in this work (Arcol 1020) was supplied by Arco Chemical and had a number-average molecular weight of 1890 g/mol with a polydispersity index of 1.1. Hydroxyl content, 1.06 mol/kg; density, 1.0 g/mL; viscosity at 25 °C, 300 mPa·s. Before use, POPG was dried for at least 3 weeks over molecular sieves and the water content checked by a Karl Fischer titration.

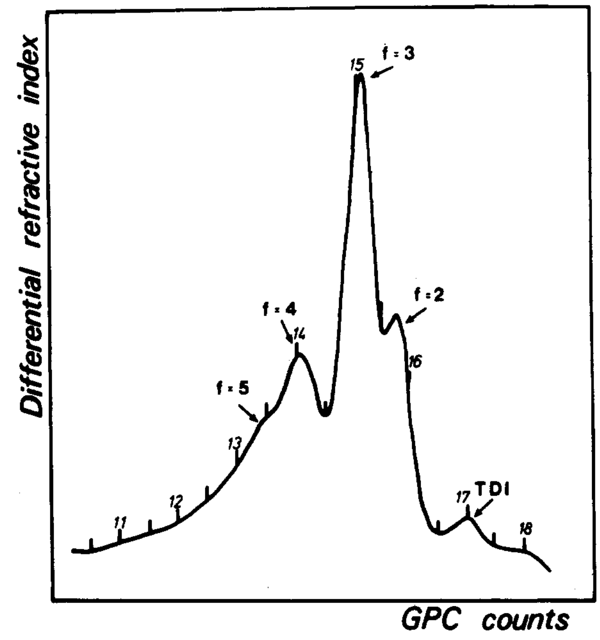
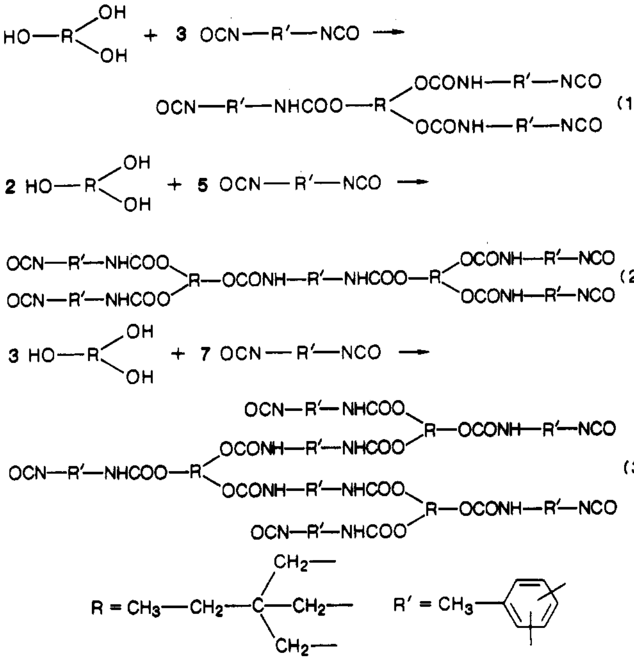


Figure 1. GPC chromatogram of L75.

Scheme I
TMP/TDI Adducts



Catalyst (OcSn). Stannous octoate (Kosmos 29 from Goldschmidt) was stored under nitrogen at low temperature and was used without further purification. Tin content, 29.1 wt %; density, 1.25 g/mol.

Solvent. Ethyl acetate, reagent grade, used as solvent was purified by distillation and kept dry over molecular sieves.

Synthesis. The synthesis of networks was performed by the following general procedure. The reagents were mixed together and rapidly stirred under dry nitrogen, stannous octoate being added last, as its catalytic action begins immediately upon contact with the polyurethane precursors. The mixture was introduced into a mold consisting of two glass plates separated by an elastomeric gasket and spring-loaded to follow the shrinkage during polymerization. The cylinders used for compression measurements were obtained in sealed glass tubes of appropriate diameter. The samples were left for 24 h at room temperature and then for 2 h at 60 °C in order to complete the reaction. The gelation occurred between 6 min and 1 h, depending upon the experimental conditions. All the compositional parameters are expressed in percentages by weight. The factor $K = [\mathrm{NCO}]/[\mathrm{OH}]$ represents the number of isocyanate functions per hydroxyl function.

Characterization Methods. Density. The density, d_0, of the various samples was determined by the density-gradient technique according to ASTM-D1505.

Sol Fraction. The soluble components in the various materials were extracted in a Soxhlet apparatus with ethyl acetate. Usually, after 11 days of continuous refluxing, no more extract was released. The sol fraction, w_s, was determined gravimetrically after evaporation of the solvent.

Gel Permeation Chromatography. The number-average molecular weights were determined by GPC on a Beckman chromatograph equipped with four μ-Spherogel columns. The mobile phase was THF. Aromatic isocyanates and poly(oxypropylene glycols), all of known molecular weight, were used for calibration. A differential refractometer and a UV spectrophotometer (λ = 254 nm) were used as detectors.

Equilibrium Swelling Degree. The equilibrium swelling degree was determined according to the conventional weighing method described elsewhere.[15] A minimum of three determinations was averaged. The equilibrium volume swelling degree, Q_v, was calculated from the equilibrium weight swelling degree, Q_w, from the relation $Q_v = 1 + (Q_w - 1)(d_0/d_s)$ where d_0 and d_s are the densities of the dry network and of ethyl acetate, respectively.

Elastic Modulus. The values of the elastic modulus, E_G, in the swollen state were obtained from uniaxial compression measurements by means of an apparatus similar to that described by Belkebir-Mrani et al.[16] A cylindrical sample is compressed between two parallel plates by turning a micrometric screw. One plate is attached to a force transducer, and the compression force is recorded versus the deformation ratio λ. The elastic modulus is related to the stress per unit base area, σ, by the equation $\sigma = E_G(\lambda - \lambda^{-2})$. All measurements were made in a thermostated cell at 23 °C.

Theoretical Part

Application of the Theory of Miller–Macosko to Our Particular System. The Miller and Macosko approach[10,11] is based on the recursive nature of the branching process and on the elementary probability law. It is assumed that all functional groups are equally reactive and react independently and that no intramolecular reactions occur during network formation. The method consists in determining the probability, P, to find a finite chain by starting from a functional group A, chosen at random, and going in a given direction. The "in" direction corresponds to looking into the chain already formed, whereas the "out" direction corresponds to looking at what has reacted with A. Let F_B^{out} be the event that B has reacted with an A group; it is equivalent to F_B^{in}. The probability of A to find a finite chain can be written

$$P(F_A^{\text{out}}) = p_A P(F_B^{\text{in}}) + 1 - p_A \qquad (1)$$

where p_A is the degree of conversion of the A groups. For plurifunctional molecules, A_f or B_g, we can write in an identical manner

$$P(F_B^{\text{out}}) = p_B P(F_A^{\text{in}}) + 1 - p_B \qquad (2)$$

and

$$P(F_A^{\text{in}}) = P(F_A^{\text{out}})^{f-1} \qquad (3)$$

where p_B is the degree of conversion of the B groups and f, the functionality of the A-type molecule.

In our case, polyurethane networks are obtained by the cross-linking polyaddition of a plurifunctional isocyanate A_f with poly(oxypropylene glycol), a difunctional precursor B_2. In fact, L75 contains species of various functionalities and f must be replaced by f_i ($2 \leqslant f_i \leqslant 5$); thus, eq 3 becomes

$$P(F_A^{\text{in}}) = \sum_{f_i=2}^{5} a_{f_i} P(F_A^{\text{out}})^{f_i-1} \qquad (4)$$

where a_{f_i} represents the molar concentration of the f_i-functional compound A_{f_i}.

On the other hand, the stoichiometric factor K is related to the extent of reaction by

$$p_B = K p_A \qquad (5)$$

Taking $p_A = p$ for simplification purposes and combining eq 1–5 give

$$Kp^2 \sum_{f_i=2}^{5} a_{f_i} P(F_A^{\text{out}})^{f_i-1} - P(F_A^{\text{out}}) - Kp^2 + 1 = 0 \qquad (6)$$

Since $P(F_A^{\text{out}}) = 1$ will always be a root, we obtain by developing the summation term

$$a_5 P(F_A^{\text{out}})^3 + (a_5 + a_4)P(F_A^{\text{out}})^2 + (a_5 + a_4 + a_3)P(F_A^{\text{out}}) + 1 - \frac{1}{Kp^2} = 0 \qquad (7)$$

From the theory of branching process, eq 7 may admit a root between 0 and 1. If there is any, it will be unique.

Above the gel point, the Miller and Macosko theory calculates the probability that a given group is not connected to the infinite network. This probability is then used to calculate for a given network the sol fraction and structural parameters, like the concentration of the cross-links and of the elastically active chains. Also, the knowledge of the sol fraction gives access to the degree of conversion, p, of the reaction.

Determination of the Sol Fraction. An A_{f_i}-type molecule is extracted when all its branches are of finite length. The probability for such an event is $P(F_A^{\text{out}})^{f_i}$; similarly for B_2, it is $P(F_B^{\text{out}})^2$. The total amount of soluble species, w_s, is thus

$$w_s = w_{B_2} P(F_B^{\text{out}})^2 + \sum_{f_i=2}^{5} w_{A_{fi}} P(F_A^{\text{out}})^{f_i} \qquad (8)$$

where $w_{A_{fi}}$ and w_{B_2} are the weight fractions of the molecules with A_{f_i} and B_2 sites, respectively.

Determination of the Extent of Reaction p. Through eq 1 and 2, $P(F_B^{\text{out}})$ may be expressed as a function of $P(F_A^{\text{out}})$:

$$P(F_B^{\text{out}}) = \frac{P(F_A^{\text{out}}) - 1}{p} + 1 \qquad (9)$$

Replacing $P(F_B^{\text{out}})$ in eq 8 and providing that $X = P(F_A^{\text{out}})$ give

$$\frac{1}{p} = \frac{\left(\dfrac{w_s - \sum_{f_i=2}^{5} w_{A_{fi}} X^{f_i}}{w_{B_2}}\right)^{1/2} - 1}{X - 1} \qquad (10)$$

Finally, by introducing this value of p in eq 7, we obtain

$$a_5 X^3 + (a_5 + a_4)X^2 + (a_5 + a_4 + a_3)X + 1 - \frac{\left[\left(\dfrac{w_s - \sum_{f_i=2}^{5} w_{A_{fi}} X^{f_i}}{w_{B_2}}\right)^{1/2} - 1\right]^2}{K(X - 1)^2} = 0 \qquad (11)$$

Equation 11 is solved by computer. The determination of the root (between 0 and 1) gives access to the extent of reaction p.

Determination of the Concentration of Cross-Links μ. A given A_{f_i} molecule constitutes a cross-link site if at least three of its functions are part of the network. Hence, the probability that A_{f_i} is a crosslink site μ of functionality m is

$$P(\mu_m, f_i) = \binom{f_i}{m} P(F_A^{\text{out}})^{f_i - m}[1 - P(F_A^{\text{out}})]^m \qquad (12)$$

where $\binom{f_i}{m} = f_i!/[m!(f_i - m)!]$ and $3 \leq m \leq f_i$ The cross-link concentration μ_m may thus be written as

$$\mu_m = \sum_{f_i=3}^{f_k} a_{f_i,0} P(\mu_m, f_i) \qquad (13)$$

where $a_{f_i,0}$ is the initial molar concentration of species A_{f_i} and f_k is the maximum functionality.

In our case, the total concentration of cross-links μ will be the sum of the individual μ_m, from $m = 3$ to 5:

$$\mu = \sum_{m=3}^{5} \mu_m \qquad (14)$$

Determination of the Concentration of Elastic Chains ν. If one assumes that every elastic chain is connected to two cross-link sites, then

$$\nu = \sum_{m=3}^{5} \frac{m}{2} \mu_m \qquad (15)$$

Deformation Behavior of a Swollen Network. Among the various theories of rubber elasticity,[17-20] only the affine[12] and the "phantom"[13] models are considered. The modulus of the affine network, $E_{\text{G,aff}}$, is given by the relation

$$E_{\text{G,aff}} = \nu RT \qquad (16)$$

For the "phantom" network, the modulus is

$$E_{\text{G,ph}} = (\nu - \mu)RT \qquad (17)$$

In fact, eq 16 and 17 are only valid for networks prepared in bulk and must therefore be corrected when the synthesis is made in solution, in order to take as reference the actual nascent state. The expressions for the affine and "phantom" modulus become

$$E_{\text{G,aff}} = \nu RT(v_2/v_{2c})^{1/3} \qquad (18)$$

and

$$E_{\text{G,ph}} = (\nu - \mu)RT(v_2/v_{2c})^{1/3} \qquad (19)$$

where v_2 is the volume fraction of the gel swollen at equilibrium and v_{2c} is the volume fraction in the nascent state.

Relationship between Elastic Modulus and Swelling Degree. By considering a polymer network swollen at equilibrium in a good solvent as a semidilute solution of a linear polymer of infinite molecular weight, de Gennes[14] has established the following relationship:

$$E_G = C_E^{9/4} \qquad (20)$$

where C_E, the segment concentration in the swollen network, is related to the network density in the dry state, d_0, and the equilibrium volume swelling degree by the ratio

$$C_E = d_0/Q_v$$

Depending on the amount of network defects, more or less deviation of the exponent from the theoretical value is observed.

Results and Discussion

Among other parameters, the morphology of the polyurethane network depends on the initial concentration of its precursors in the reaction medium (hereafter referred to as %PUR) and also on the value of the ratio $K = [\text{NCO}]/[\text{OH}]$. The %PUR was varied from 15 to 80 and K from 0.85 to 1.45. The various syntheses were made in ethyl acetate which has been shown to behave like methyl methacrylate[5] toward the polyurethane network and its precursors. The catalyst concentration was 1 wt % with regard to the total weight.

Table II
Characterization of the Polyurethane Networks Prepared at Various Dilutions in Ethyl Acetate with 1% Stannous Octoate[a]

%PUR	K	d_0, g/mL	w_S, %	Q_V	$10^{-5}E_G$, Pa
15	0.85	1.0887	20	25.84	0.044
15	1.00	1.0890	3.4	11.18	0.35
15	1.07	1.1005	3.0	10.48	0.37
15	1.15	1.1040	3.2	10.45	0.39
15	1.30	1.1072	3.6	9.80	0.41
35	0.85	1.0772	8.4	10.10	0.47
35	1.00	1.0808	1.4	5.88	0.79
35	1.07	1.0881	0.9	5.85	1.40
35	1.15	1.0911	2.4	6.10	1.12
35	1.30	1.1008	2.4	6.49	1.12
35	1.45	1.1028	0.9	6.62	0.68
55	0.85	1.0739	6.6	7.04	1.05
55	1.00	1.0805	1.0	4.65	2.02
55	1.07	1.0866	0.7	4.74	2.32
55	1.15	1.0893	1.2	4.81	2.03
55	1.30	1.0978	1.3	5.15	1.80
65	0.85	1.0658	6.1	6.58	1.12
65	1.00	1.0802	1.1	4.11	2.55
65	1.07	1.0839	0.3	4.03	2.64
65	1.15	1.0870	0.3	4.27	2.20
65	1.30	1.0911	0.3	4.41	2.23
65	1.45	1.0963	0.8	5.13	1.57
80	0.85	1.0609	9.1	6.17	1.32
80	1.00	1.0683	1.9	4.13	2.83
80	1.07	1.0724	0.5	3.68	3.54
80	1.30	1.0864	0.6	4.18	2.73

[a] d_0 is the density at 23 °C; w_S is the sol fraction; Q_V is the equilibrium volume swelling degree; E_G is the experimental elastic modulus.

The networks were characterized in three ways: sol fraction, swelling degree, and compression modulus measurements. Then the experimental results were utilized in the above described theoretical approaches.

Network Characterization. Solvent Extraction. The experimental results are reported in Table II and in Figure 2. It appears that the excess of reactant in off-stoichiometric conditions is less integrated into the network for POPG than it is for L75. The higher extent of NCO fixation onto the network ($K > 1$) may be ascribed to the higher functionality, so that the occurrence of other reactions is not necessary to explain the experimental results. Ilavsky and Dusek[21] and Macosko and Benjamin[22] have obtained the same extraction curves on polyurethane networks and poly(dimethylsiloxane) networks, respectively. The former authors assign the deviation from the theoretical curve to allophanate formation, whereas the latter give an explanation similar to ours.

At low K values, the amount of soluble material, w_s, i.e. unfixed species, is high whatever the PUR content, reaching 20% for the sample prepared in presence of 85% of solvent. w_s decreases markedly when K is between 1.05 and 1.10. The actual concentration ratio seems to correspond to about 7% more isocyanate functions than the stoichiometric amount. It is possible that, due to their sensitivity to humidity, a certain number of NCO functions are destroyed prior to urethane formation. As expected, the highest concentrations in PUR yield the least quantity of extractable species, as the probability of encounter between isocyanate and hydroxyl groups increases.

Analysis of the Sol Fraction. The extractable materials were analyzed by GPC and UV spectroscopy.

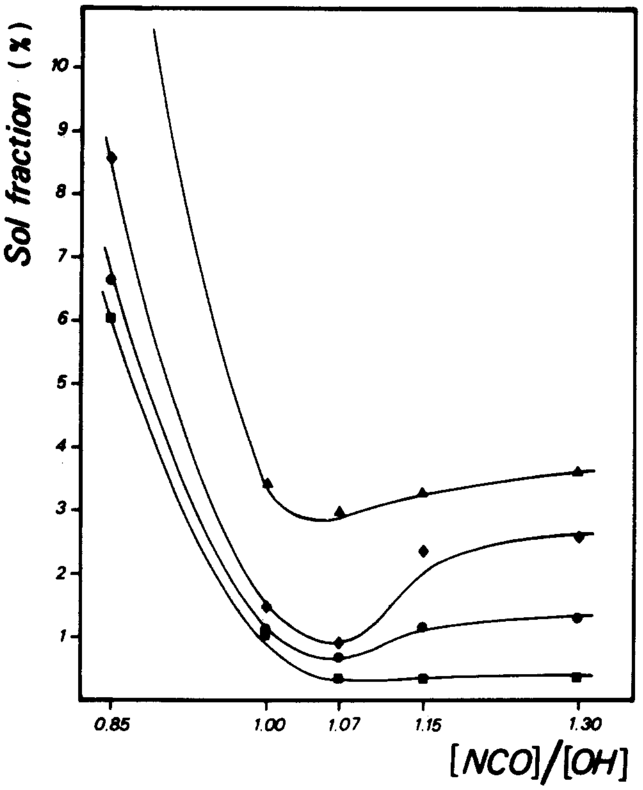


Figure 2. Amount of soluble material extracted from various PURs as a function of the ratio K = [NCO]/[OH]. Networks prepared in 35% (■), 45% (●), 65% (◆), and 85% (▲) ethyl acetate with 1% OcSn at 23 °C.

Though the specific nature of the different species cannot be deduced directly, these techniques yield more quantitative results than IR spectroscopy: GPC provides the number of peaks and their molecular weights, and UV spectroscopy allows calculation of the aromatic content present in the material through L75. Note that even in the absence of a shoulder, a GPC peak may represent more than one species, if their hydrodynamic volume is similar.

The analysis of the soluble extract by GPC shows the presence of at most seven peaks which appear always at the same GPC counts for all the samples. They correspond to those found for L75 and for POPG; hence, the sol fraction contains both precursors, but a combination between them cannot be excluded as two peaks appear above 2000 g/mol. Investigations on the actual chemical nature of the sol fraction are still on the way. Attempts have been made by examining the possible changes of L75, POPG, and stannous octoate when subjected to the same refluxing conditions as for an extraction experiment on a network. After 11 days in boiling ethyl acetate, POPG is not degraded and no linear polycondensation occurs. Also, the peak corresponding to OcSn, which appears in a different region of the GPC curve than L75 and POPG, is not shifted. On the other hand, L75 is modified in boiling ethyl acetate, see Table III. Apart the adducts already present in L75, and assumed to have remained unchanged, two new peaks, the same as in the sol fraction, corresponding to species of higher molecular weights appear after 4 h and 3.5 days of solvent refluxing. Both have formed at the expense of all the initial adducts. It seems that L75 undergoes recombinations until the NCO functions are consumed. The numerous reactions possible with isocyanate make difficult the determination of the actual chemical nature of the new derivatives and are not considered here.

Swelling Measurements. The extent to which a network swells in a given solvent is inversely proportional to the segment concentration. The equilibrium swelling degree by volume, Q_v, in ethyl acetate is reported in Table II and Figure 3 for various PUR samples. Q_v decreases steadily when the concentration of polyurethane increases up to 80%; this is an indication that tighter networks are formed at lower dilutions. Whatever the PUR content, Q_v goes through a minimum around K = 1.07. For lower K values, the excess in POPG chains explains the lack of cross-links. But above K = 1.07, the number of isocyanate functions in the reaction medium is at least sufficient to maintain the same Q_v value, so that the slight increase in Q_v is not obvious at first sight. An increase in Q_v may correspond to a higher molecular weight between cross-links, which signifies that a certain number of junction points have in fact a functionality of less than 3, caused by the large excess of isocyanate groups over hydroxyl groups.

Compression Measurements. The compression modulus is related to the cross-link density of a network. The equilibrium elastic modulus of swollen PUR samples, E_G, appears in Table II and in Figure 4. It increases as the %PUR increases and has a maximum value for K = 1.07, so that these results corroborate the ones obtained from

Table III
Compositional Change of L75 in Boiling Ethyl Acetate

	wt %				postulated adducts	
M_n[a]	0 day	0.2 day	3.5 days	11 days	M_n[b]	TMP/TDI
460	17	12	12	12		
660	43	30	22	22	656	1:3
1280	23	15	15	15	1138	2:5
1740	17	15	15	15	1620	3:7
2820		28	17	17		
4850			19	19		

[a] By GPC, in g/mol. [b] Calculated.

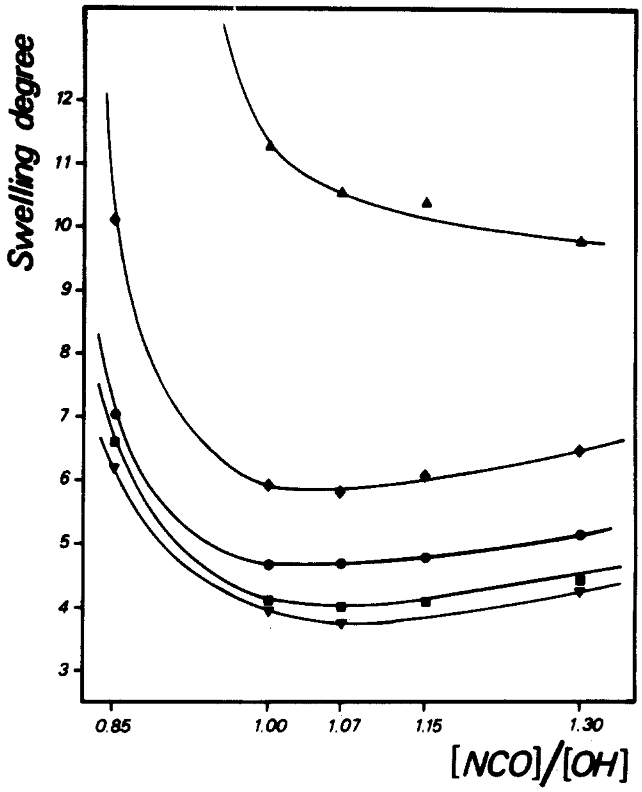


Figure 3. Equilibrium swelling degree by volume as a function of the ratio K = [NCO]/[OH]. Networks prepared in 20% (▼), 35% (■), 45% (●), 65% (◆), and 85% (▲) ethyl acetate with 1% OcSn at 23 °C.

Table IV
Structural Parameters of the Polyurethane Networks Prepared at Various Dilutions in Ethyl Acetate with 1% Stannous Octoate[a]

%PUR	K	v_{2c}	p, %	$10^2\nu_0$, mol/L	$10^2a_{f,0}$, mol/L	$10^2\nu$, mol/L	$10^2\mu$, mol/L
15	0.85	0.127	88.1	5.00	1.84	0.60	0.38
15	1.00	0.127	89.7	5.81	2.25	2.02	1.24
15	1.07	0.126	86.2	5.74	2.70	2.03	1.25
15	1.15	0.126	82.0	5.67	2.86	1.91	1.18
15	1.30	0.125	75.6	5.47	3.49	1.91	1.19
35	0.85	0.310	94.7	14.47	5.41	3.36	2.09
35	1.00	0.309	92.9	14.03	6.16	6.45	3.92
35	1.07	0.308	89.8	13.87	6.52	6.79	4.13
35	1.15	0.308	83.0	13.67	9.91	5.10	3.15
35	1.30	0.306	76.8	13.30	7.60	4.83	3.00
35	1.45	0.305	74.0	12.93	8.24	6.18	3.81
55	0.85	0.506	96.4	23.55	8.80	6.41	3.96
55	1.00	0.504	93.9	22.87	10.05	11.34	6.87
55	1.07	0.503	90.3	22.63	10.64	11.61	7.04
55	1.15	0.502	84.8	22.28	11.25	10.03	6.14
55	1.30	0.500	78.3	21.71	12.40	9.38	5.78
65	0.85	0.611	96.9	28.20	10.54	8.05	4.96
65	1.00	0.607	93.6	27.54	12.11	13.39	8.11
65	1.07	0.607	91.8	27.22	12.80	15.68	9.46
65	1.15	0.606	87.4	26.83	13.56	15.13	9.17
65	1.30	0.605	81.0	26.11	14.92	14.96	9.11
65	1.45	0.604	74.3	25.45	16.22	12.52	7.71
80	0.85	0.772	94.2	35.49	13.26	7.78	4.84
80	1.00	0.771	91.9	34.59	15.20	14.67	8.95
80	1.07	0.770	91.0	34.19	16.08	18.48	11.18
80	1.30	0.768	79.8	33.00	18.86	16.76	10.26

[a] v_{2c} is the concentration of polymer segment in the nascent state; p is the theoretical conversion ratio of the NCO groups; ν_0 is the initial concentration of POPG; $a_{f,0} = \sum_{f_i=3}^{5} a_{fi,0}$ is the initial concentration of the cross-linking species of L75; ν is the concentration of the elastically active network chains; μ is the concentration of chemical cross-links.

swelling measurements, as well as those from soluble species extraction.

Corroboration through Theoretical Approaches. The above experimental results have been utilized to evaluate our polyurethane networks with regard to different theoretical approaches concerning polymer networks.

Degree of Conversion and Structural Parameters. The synthesis of the present PUR consists of a succession of end-linking reactions between the NCO groups of L75 and the OH groups of POPG. Such a polyaddition gives networks with rather well-defined structure and minimum defects. However, the variation of K, as well as the fact that L75 contains species with various functionalities, introduces additional defects and also an uncertainty about the actual number of junctions starting from a given cross-linking site. Thus, it is all the more important to be able to evaluate precisely the actual structure of our PUR and to calculate their effective structural parameters.

The values of p, μ, and ν have been determined by solving eq 11 and 10, 14, and 15, respectively. The results, listed in Table IV, show that a 100% conversion is never attained under our experimental conditions: the maximum value is 97% in near-stoichiometric situations. At a constant K value, as the concentration in PUR increases, p, μ, and ν increase. When K varies from 0.85 to 1.45 for a given %PUR, the extent of the reaction decreases. For $K > 1.07$, this result shows that an excess of isocyanate does not contribute to the cross-link density, as stated by other authors.[21] The values of μ and ν go through a maximum for $K = 1.07$ (Figure 5), thus corroborating the results obtained by swelling and compression measurements: networks formed under these conditions have the least defects. However, the comparison of the values of μ and ν with their corresponding initial amounts, $a_{f,0}$ and ν_0 (Table IV), indicates at first sight that, even in this case, the polyurethane network is far from an ideal network.

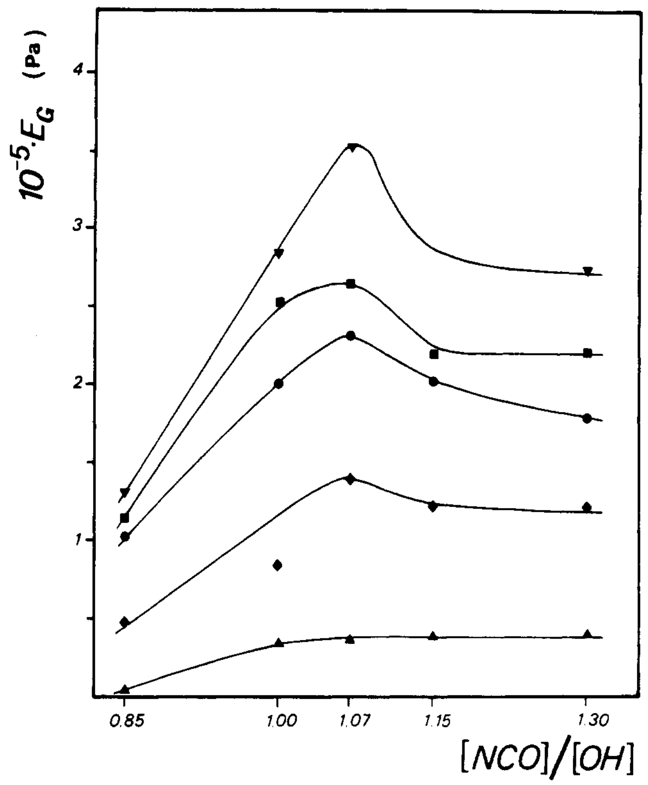


Figure 4. Elastic modulus, E_G, as a function of the ratio K = [NCO]/[OH]. Networks prepared in 20% (▼), 35% (■), 45% (●), 65% (◆), and 85% (▲) ethyl acetate with 1% OcSn at 23 °C.

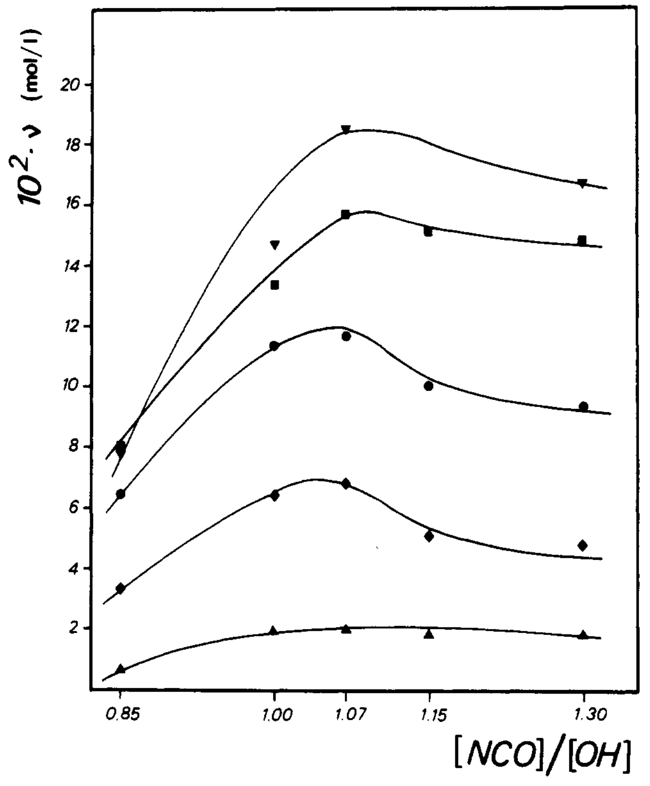


Figure 5. Concentration of elastically active chains, ν, as a function of the ratio K = [NCO]/[OH]. Networks prepared in 20% (▼), 35% (■), 45% (●), 65% (◆), and 85% (▲) ethyl acetate with 1% OcSn at 23 °C.

Table V
Elastic Modulus of the Polyurethane Networks Prepared at Various Dilutions in Ethyl Acetate with 1% Stannous Octoate[a]

%PUR	K	υ_2	υ_{2c}	$10^{-5}E_G$, Pa exptl	affine	"phantom"
15	0.85	0.039	0.127	0.044	0.098	0.036
15	1.00	0.089	0.127	0.35	0.44	0.17
15	1.07	0.095	0.126	0.37	0.46	0.18
15	1.15	0.096	0.126	0.39	0.43	0.16
15	1.30	0.102	0.125	0.41	0.44	0.17
35	0.85	0.099	0.310	0.47	0.56	0.21
35	1.00	0.170	0.309	0.79	1.30	0.51
35	1.07	0.171	0.308	1.40	1.37	0.54
35	1.15	0.164	0.308	1.12	1.02	0.39
35	1.30	0.154	0.306	1.12	0.95	0.36
35	1.45	0.151	0.305	0.68	0.74	0.28
55	0.85	0.142	0.506	1.05	1.03	0.39
55	1.00	0.215	0.504	2.02	2.10	0.83
55	1.07	0.211	0.503	2.32	2.14	0.84
55	1.15	0.208	0.502	2.03	1.84	0.71
55	1.30	0.194	0.500	1.80	1.68	0.65
65	0.85	0.152	0.611	1.12	1.24	0.48
65	1.00	0.243	0.607	2.55	2.43	1.32
65	1.07	0.248	0.607	2.61	2.86	1.13
65	1.15	0.234	0.606	2.20	2.73	1.08
65	1.30	0.227	0.605	2.23	2.65	1.04
65	1.45	0.195	0.602	1.57	2.11	0.81
80	0.85	0.162	0.772	1.32	1.14	0.43
80	1.00	0.242	0.771	2.83	2.45	0.96
80	1.07	0.272	0.770	3.54	3.21	1.27
80	1.30	0.239	0.768	2.73	2.79	1.12

[a] υ_2 and υ_{2c} are the concentrations of the gel swollen at equilibrium and of the polymer segment in the nascent state, respectively.

This conclusion will be examined again later, together with the other results.

Elastic Behavior. In Table V, the experimental modulus obtained by compression measurements is compared to the moduli calculated through eq 18 and 19. The experimental values are very close to those obtained from the affine network model and clearly far from the "phantom" network model (Figure 6). Therefore, it can be seen that the degree of dilution of the reaction medium does not influence the behavior of the polyurethane gels. Such a result may be related to the specific nature of the cross-linking agent: the molecular weight of its different species is high compared to that of POPG, and the presence of aromatic cycles confers to them a pronounced rigidity. Moreover, the concentration of L75 represents about 30% of the total weight of the polyurethane. For all these reasons, the fluctuations of the cross-linking sites under a small deformation should be very limited, which may explain the out-spoken affine character of such networks.

Relationship between Elastic Modulus and Swelling Degree. The values of Q_v and E_G (Table II) have been utilized to test eq 20 for our PUR samples. For a given K, log E_G versus log C_E plots yield a straight line (Figure 7) and the following relationships have been obtained: for $K = 0.85$, $E_G = 13.2 \times 10^6 C_E^{2.70}$; for $K = 1.07$, $E_G = 5.5 \times 10^6 C_E^{2.23}$; for $K = 1.30$, $E_G = 5.9 \times 10^6 C_E^{2.30}$, with a correlation factor of 0.995–0.997. For $K = 1.07$, the exponent is very close to the theoretical value of $^9/_4$; also, for higher K's, a slope of 2.30 still indicates a network with rather few defects. However, the situation changes drastically when the reaction medium is rich in POPG chains ($K < 1$): the deviation from the theoretical value becomes important, showing that only imperfect networks can be formed in such experimental conditions.

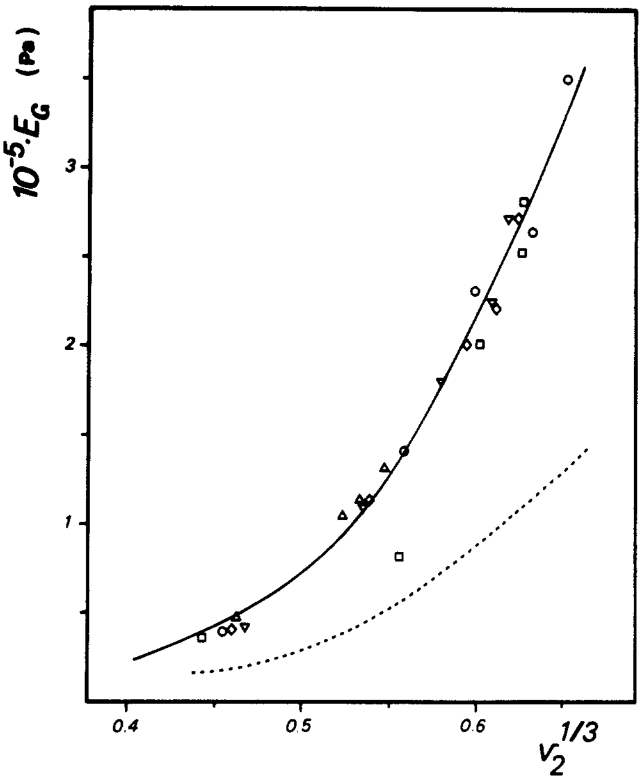


Figure 6. Elastic modulus, E_G, as a function of the polymer volume fraction, υ_2, for PUR prepared with 1% OcSn in ethyl acetate at 23 °C. K = 0.85 (△), 1.00 (□), 1.07 (○), 1.15 (◇), and 1.30 (▽). (—) Curve calculated according to the affine model; (---) curve calculated according to the "phantom" model.

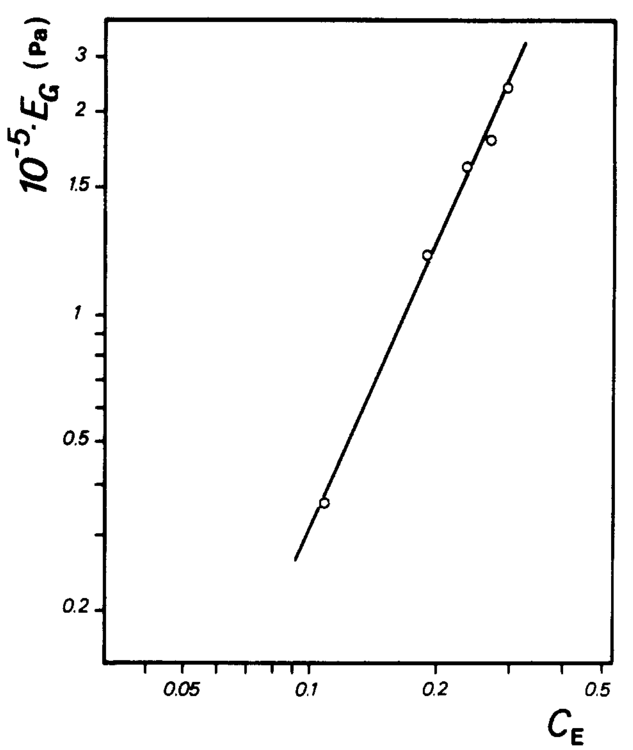


Figure 7. Elastic modulus, E_G, as a function of the segment concentration, C_E, for K = 1.07; slope = 2.23.

General Discussion

The three experimental approaches utilized to study the network defects of polyurethane networks are independent. All show that the best networks, in terms of low sol fraction, low swelling degree, and high modulus, are formed for $K \sim 1.07$ at rather high concentrations of PUR precursors in the reaction medium. By themselves, these results are sufficient to provide a relative classification of the samples obtained in different experimental conditions. It occurs that the approach through theoretical considerations elaborated by different authors corroborates well these conclusions. Thus, de Gennes' concept, applied to the experimental E_G and Q_v, yields values which again show that the least network defects arise by using $K \sim 1.07$. It is, however, interesting to note that the scaling law concept is general enough to apply well also to the present polyurethane system. In this view, an absolute classification including any tridimensional structure is possible. By utilizing the Miller–Macosko theory, the maxima of μ and ν also confirm the value of $K = 1.07$. As already pointed out, these values are far from the initial concentration $a_{f,0}$ and ν_0, which is inconsistent with the above conclusions that the networks have rather few defects.

But it should be kept in mind that ν refers to all the elastic chains, whereas ν_0 represents the number of initially present POPG chains. A direct comparison between ν and ν_0 infers that at best half of the initial POPG chains are integrated into the network by their two extremities, a hypothesis which is also in contradiction with the very low amount of extractable species. The most likely assumption is that, in fact, many junction points are difunctional, therefore leading to chain extensions with several POPG molecules linearly bonded. Also, by taking into account the pendent chains, the apparent discrepancy between ν and ν_0 (and μ and $a_{f,0}$) is explained. Finally, it can be noted that the various approaches utilized to investigate a series of polyurethane networks yield quite coherent information.

Conclusion

The above study provides a quite precise estimation of the structure of a polyurethane network synthesized in various conditions. As PUR plays the role of a host network toward poly(methyl methacrylate) in PUR/PMMA IPNs, the knowledge of its actual nature is indispensable for the interpretation of certain experimental facts observed during the building up of the second network, as well as for the final properties of IPNs. Once relationships between synthesis and properties have been established, the a priori choice of a host network of adapted structure will also be possible.

It results from the literature that for a given concentration, the properties of an IPN do not vary much with the usual parameters of synthesis. Perhaps varying the number of defects of the first-formed network will be the only way to impart custom-made properties to an IPN without changing the relative amount of the two components.

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Registry No. (Desmodur L75)(POPG) (copolymer), 71599-33-2.

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