

Swelling Properties of Urethane Elastomers and Their Bearing on Microphase Separation

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Synopsis

Several polyurethanes were prepared from polyethylene adipate glycol, 4,4'-diphenylmethane diisocyanate, 1,4-butanediol, and 3,3'-dichloro-4,4'-diaminodiphenylmethane. The temperature dependence of swelling and dynamic mechanical properties were determined. Analysis of the data shows that microphase separation leaves its mark on the swelling properties and that some information on the extent and perfection of microphase separation can be obtained from swelling. The conclusions were found to be in general agreement with the modulus-temperature relationships.

INTRODUCTION

It has long been the practice in the investigations of polymer networks to determine the number of elastically effective chains to obtain a measure of the crosslinking density. One method of determining the quantity is based on equilibrium swelling measurements. The calculations of crosslinking density by this method stem from the statistical theory of rubber elasticity.

In the case of polyurethanes, however, such an approach may lead to doubtful results. Very few if any real polymer networks follow the ideal rubber elasticity predictions, but for polyurethanes the deviations from the theory are especially remarkable.^{2,3} The deviations result from a very peculiar polyurethane structure. It is well known that urethane elastomer is a block copolymer of the $(AB)_n$ type. The materials generally consist of a polyether or polyester soft segment and a hard segment usually formed by the reaction of a diisocyanate with a glycol or a diamine. Strong polar interactions in the systems can lead to a segregation of the unlike blocks into separate domains. The segregation is qualitatively well established by small-angle x-ray measurements,⁴ and the domains are seen from electron micrographs.⁵ The inhomogeneous structure of polyurethanes is in contradiction with the basic assumption of the statistical theory of rubber elasticity stating that the theory is applicable only to homogeneous systems.

Taking into account an estimate⁶ of the energies of interaction common in the urethane chemistry groups, one can expect the interactions between hard segments to be so strong that the domain structure may remain even in the swollen state, especially when swelling is done with poor or moderate solvents.

This work was undertaken to show that swelling results are affected by microphase separation and that some information on the perfection of separation can be extracted from the results as well. Together with the already mentioned work on thermoelastic properties of urethane elastomers,³ this work is intended to stress some thermodynamic consequences of microphase separation.

EXPERIMENTAL

Materials

The materials used in this study were obtained by a prepolymer route. The prepolymers were prepared from poly(ethylene adipate) diol (PEA) of molecular weight 2000. After PEA had been stripped of moisture and gas (385 K, 2 hr., 3 Torr), the prescribed amount of 4,4'-diphenylmethane diisocyanate (MDI) was added to the diol to obtain the prepolymer (395 K, 30 min). When the isocyanate-diol reaction had been completed, either 1,4 butanediol (BDO) or 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) was added to the prepolymers and the reaction mixture was poured into a centrifuge (395 K). After 10 to 15 min, the film was removed and the curing reaction was completed in an oven (395 K, 24 hr). The various samples examined and their molar compositions are shown in Table I.

Swelling Measurements

All samples were selected from films in which no imperfection due to air bubbles were observed. The equilibrium degree of swelling q (swollen:dry volume) in nitrobenzene (reagent grade) and dibutyl phthalate (distilled over CaCl_2) in the temperature range of 300–415 K was determined by equilibrating small pieces of polymers (0.5 g) in excess solvent for 70 hr. The pieces were then blotted and weighed in a closed vessel. The samples from dibutylphthalate were washed with acetone prior to drying. The swelling degree was calculated assuming additivity of polymer and solvent volumes. The densities of polyurethanes at 298 K were determined by hydrostatic weighing technique in water. Densities at the temperatures used in swelling were determined for the two solvents, while for the polymers the coefficients of thermal expansion found previously³ were employed. In nitrobenzene the amount of soluble material was found to be 1.5%–2.0%. The soluble compounding material was taken into account prior to computing the equilibrium degree of swelling.

The obtained swelling degrees are presented graphically in Figures 1, 2, and 3.

TABLE I
Compositions of Investigated Samples

Polymer	PEA/MDI/BDO	PEA/MDI/MOCA	w_h^a
Pu-2	1.00/2.75/1.43		0.29
Pu-3	1.00/3.50/2.08	×	0.35
Pu-4	1.00/4.25/2.76		0.39
Pu-5	1.00/5.00/3.57		0.44
Pu-12		1.00/2.75/1.35	0.26
Pu-13		1.00/3.50/2.08	0.43
Pu-14	×	1.00/4.25/2.76	0.46
Pu-15		1.00/5.00/3.45	0.52

^a w_h is the weight fraction of hard segments.

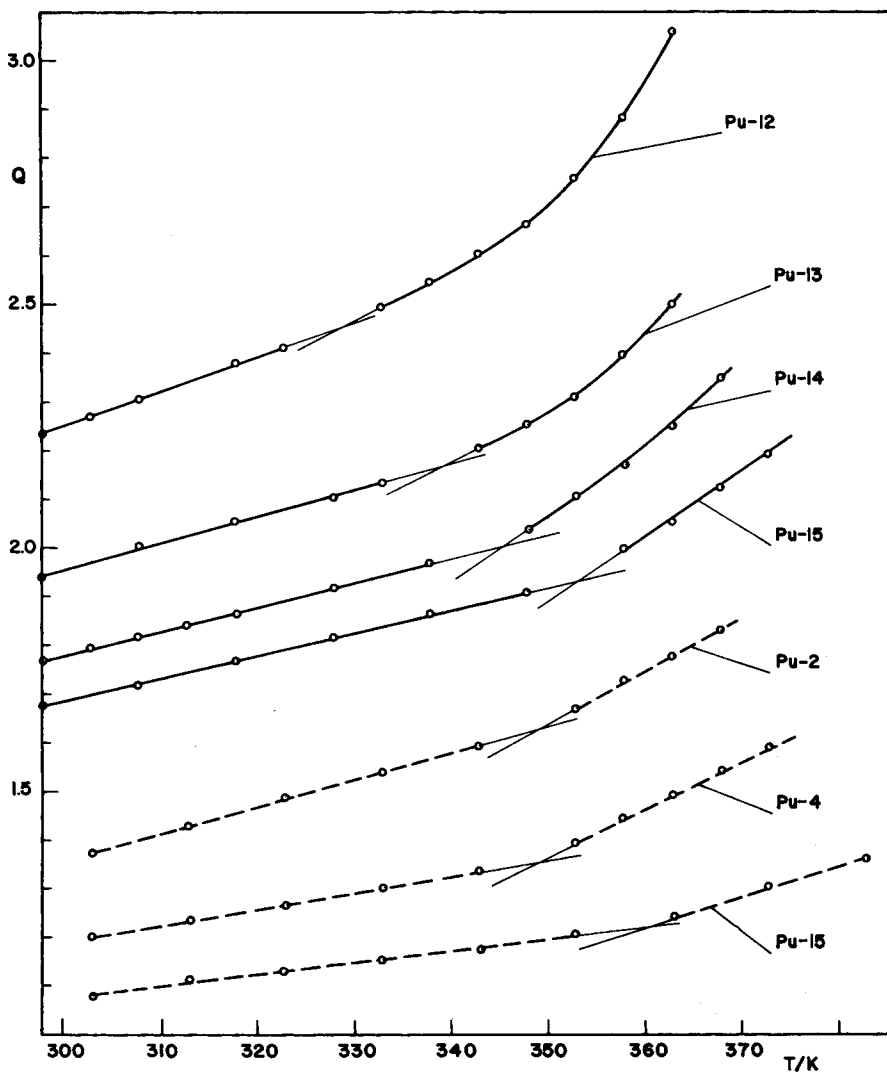


Fig. 1. Temperature dependence of swelling for indicated polyurethanes in nitrobenzene (—) and dibutylphthalate (---).

Dynamic Measurements

The measurements were kindly performed for us by Dr. E. Balcerzyk from IWCh Lodz on a Toyo Rheovibron direct-reading viscoelastometer DDV. Dynamic mechanical properties of unswollen samples were measured at 110 Hz. The samples were heated at a rate of 1–2 deg/min.

The storage moduli E' of the investigated samples are presented in Figures 4 and 5.

DISCUSSION

From Figures 1, 2, and 3 it is easily seen that for all the investigated polymer-solvent systems the equilibrium swelling degree increases with temperature (endothermic mixing) and that after a certain temperature is reached the rate

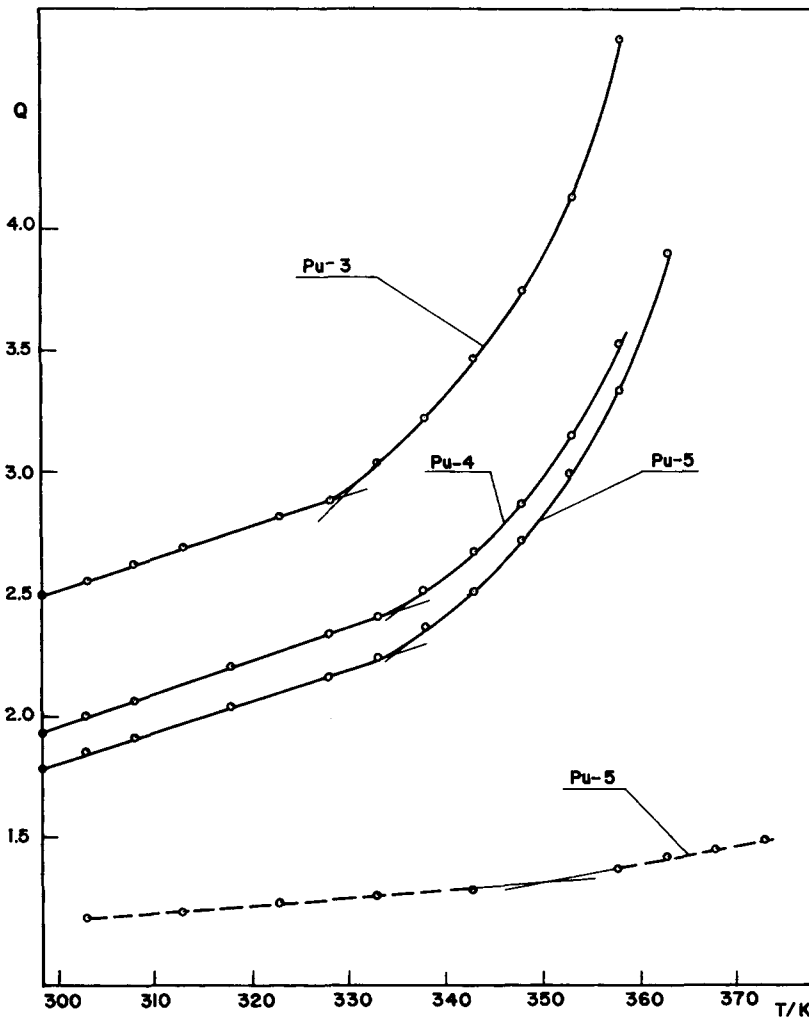


Fig. 2. Temperature dependence of swelling for indicated polyurethanes in nitrobenzene (—) and dibutylphthalate (- - -).

of the increase is remarkably higher. In our opinion it may reflect the existence of microphase separation, even in the swollen state, if the temperature is sufficiently low. In higher temperature regions the microphase separation disappears, which results in more efficient swelling.

As is known, phase separation is a consequence of the interactions between hard and soft blocks which lead to positive enthalpy terms not counterbalanced by negative entropy terms. In a sufficiently high temperature, however, the entropy term $-T\Delta S$ may become negative enough to outweigh the positive enthalpy of mixing. Above this temperature the phase separation does not take place at all. The critical separation temperature T_s , already defined for block copolymers by Leary and Williams,^{7,8} can be reduced by the presence of solvent to an extent depending on the nature of the solvent. For the investigated systems the separation temperatures are collected in Table II. They were obtained at the intersections of tangents drawn to the lines q versus T . The presented data

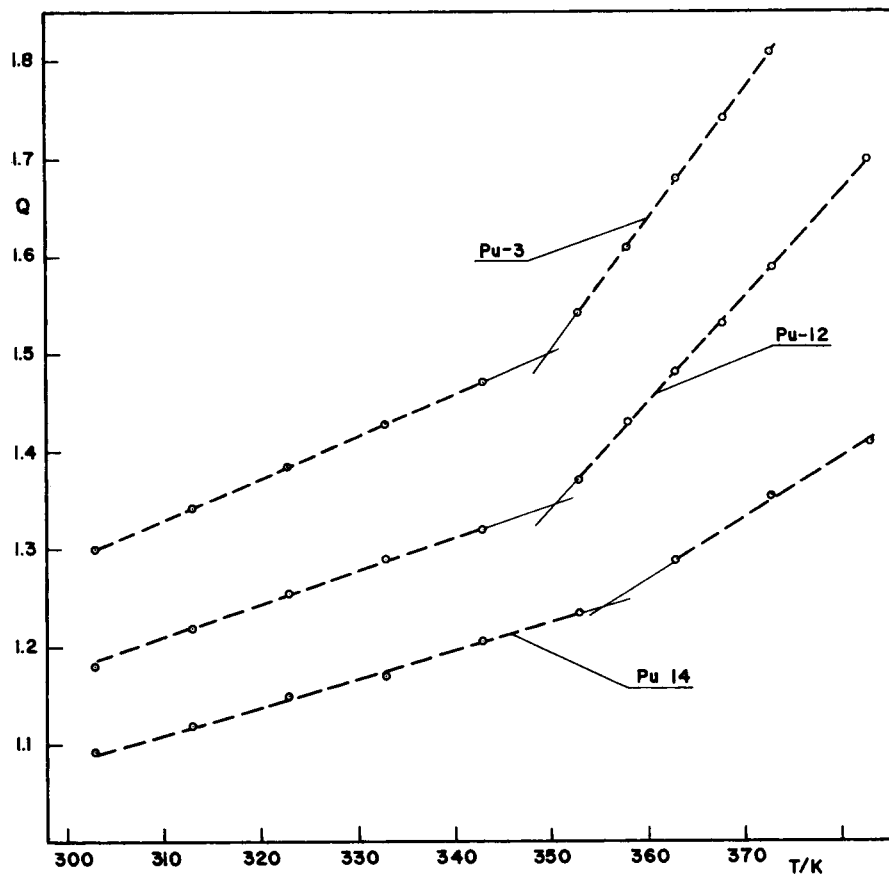


Fig. 3. Temperature dependence of swelling for indicated polyurethanes in dibutylphthalate.

TABLE II
Thermodynamic Data of the Investigated Systems

Polymer	Nitrobenzene		Dibutylphthalate	
	T_s/K	$\Delta\bar{H}_A$, kJ/mole	T_s/K	$\Delta\bar{H}_A$, kJ/mole
Pu-2	—	—	349	2.22
Pu-3	330	0.31	350	2.28
Pu-4	335	1.10	350	2.60
Pu-5	336	1.65	351	2.77
Pu-12	331	0.18	352	2.98
Pu-13	335	0.24	—	—
Pu-14	345	0.44	355	3.21
Pu-15	353	0.51	360	3.04

show that nitrobenzene depresses the separation temperature more efficiently when compared to dibutyl phthalate. It is also seen that the greater the hard segment concentration, the higher the separation temperature.

A deeper insight into the phase separation can be gained by analyzing changes in the Flory-Huggins interaction parameter χ and in the partial molar enthalpy of dilution of the solvents, $\Delta\bar{H}_A$. The interaction parameters were found from

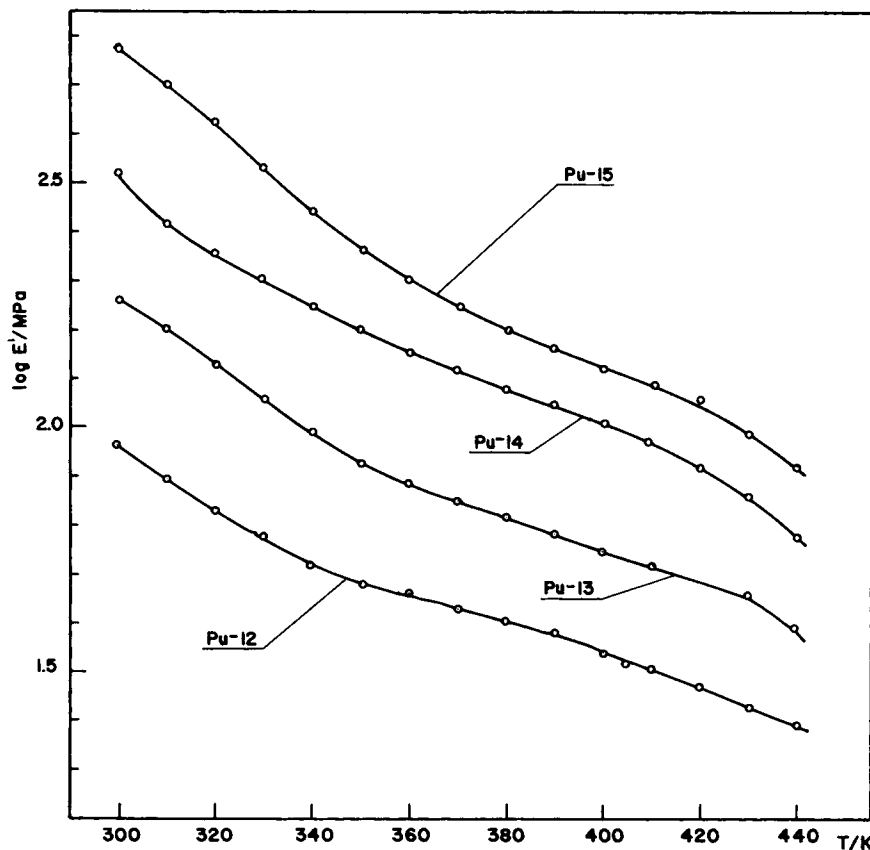


Fig. 4. Temperature dependence of dynamic mechanical properties of MOCA-based polyurethanes.

the Flory–Rehner expression for the temperature coefficient of swelling.⁹ The expression was used in the following form:

$$\chi = \frac{0.8333 + 0.8889q^{-1} + 0.9167q^{-2} + 0.9333q^{-3}}{1.6667 + [q/(\partial q/\partial T)]T} \quad (1)$$

Typical results obtained from eq. (1) are shown in Fig. 6. The striking fact which emerges from the figure is a rapid increase in the interaction parameter values after a certain (i.e., T_s) temperature is reached.

The interaction parameter has been used as a measure of the “goodness” of a solvent for a given polymer–solvent systems. This means that the lower the value of the parameter, the better the solvent. The rapid increase of the interaction parameter observed in the investigated systems means that the solvents get worse at sufficiently high temperatures, i.e., at T_s . Apparently below the separation temperature the polymer–solvent interactions are mainly the soft phase–solvent interactions, while above the temperature a contribution from the hard polar segments becomes remarkable due to disruption of the hard domains. The increase in the values of the interaction parameter is smaller for nitrobenzene systems which is a consequence of higher nitrobenzene compatibility to the hard urea or urethane segments.

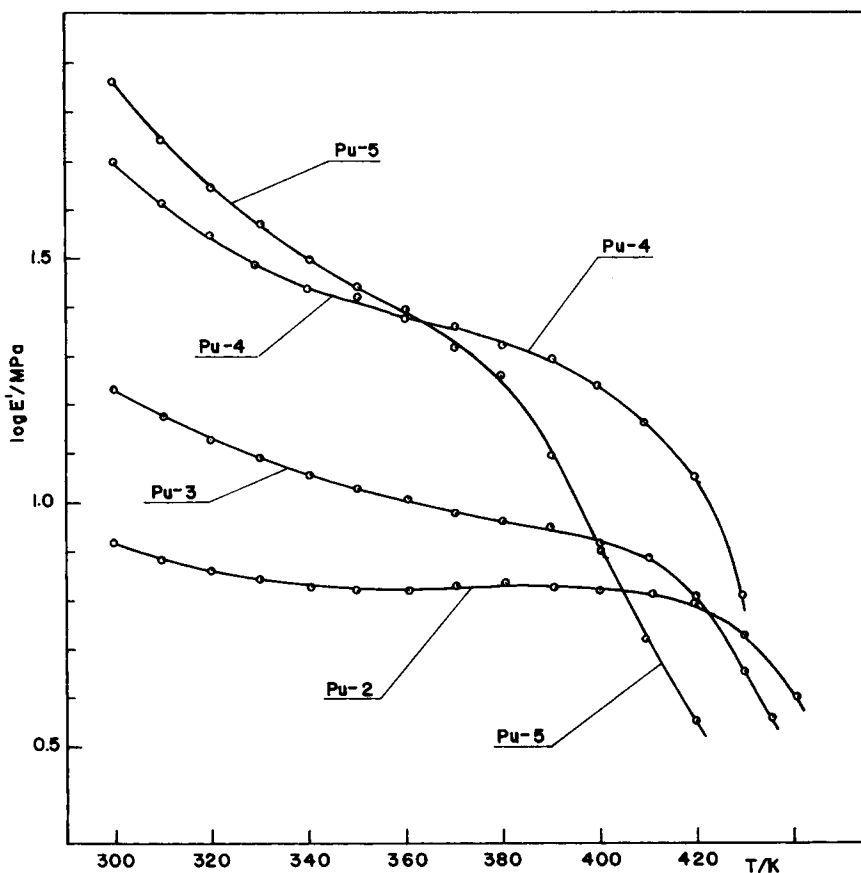


Fig. 5. Temperature dependence of dynamic mechanical properties of BDO-based polyurethanes.

To find the partial molar enthalpy of dilution values, we assume that the chemical potential of solvent in crosslinked polymers is described by the well-known Flory-Huggins formula¹

$$\mu_A - \mu_A^0 = RT[\ln(1 - q^{-1}) + q^{-1} + \chi q^{-2}] \quad (2)$$

For the ideal systems, however, $\mu_A - \mu_A^0 = RT \ln X_A$, where X_A , the mole fraction of solvent, equals $N_A/(N_A + N_B)$. For a crosslinked swollen polymer, the number of polymer molecules N_B may be put at 1. As a result, $X_A \cong 1$ and $\ln X_A \cong 0$. Thus eq. (2) may be treated as an approximate equation for the excess chemical potential of solvent, $(\mu_A - \mu_A^0)^E$. From the Gibbs-Helmholtz equation, it also follows that $\partial(\mu_A - \mu_A^0)^E/\partial T = -\Delta\bar{H}_A/T^2$. After expanding the logarithmic term in eq. (2) in series, the following is finally obtained:

$$\frac{\partial[Rq^{-2}(\chi - 0.5)]}{\partial(1/T)} = \Delta\bar{H}_A \quad (3)$$

Despite the admitted shortcomings of the Flory-Huggins formula, we believe that we can quite safely draw conclusions from $\Delta\bar{H}_A$ values obtained by using eq. (3) since we are not interested in their absolute magnitudes but rather in their trends with temperature. Being interested in relative trends makes also more

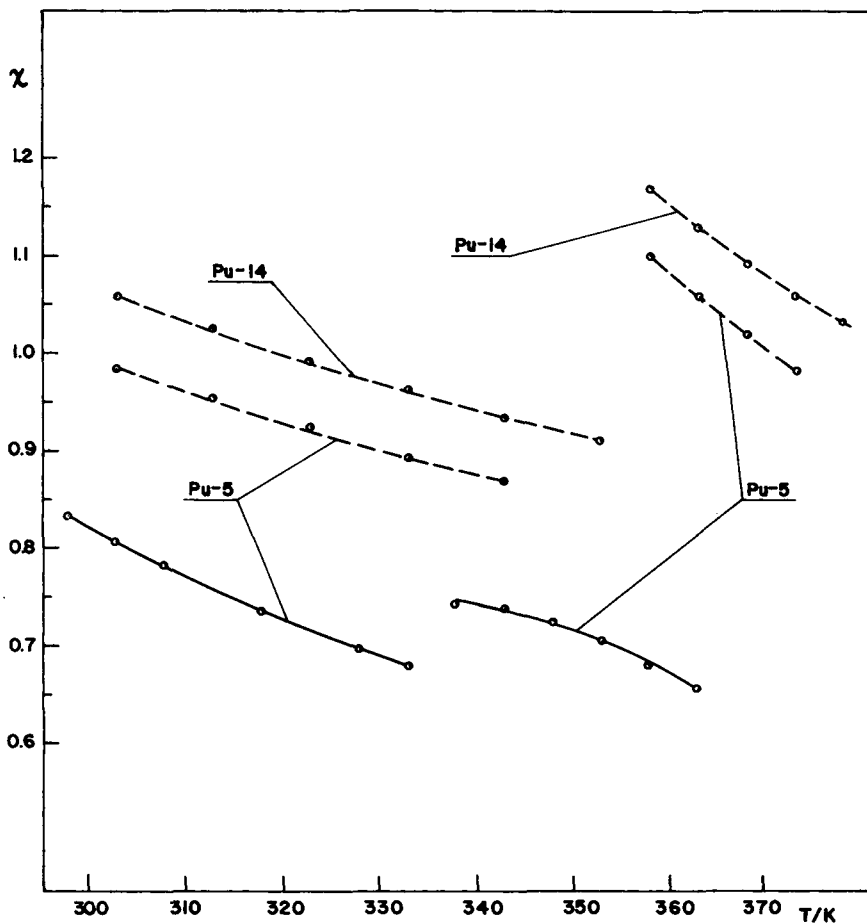


Fig. 6. Temperature dependence of the interaction parameter for selected polyurethane-solvent systems: (—) nitrobenzene; (---) dibutylphthalate.

justifiable the neglect of the possible concentration dependence of $\Delta\bar{H}_A$ in the discussion.

Figure 7 shows a typical plot of $Rq^{-2}(\chi - 0.5)$ versus $1/T$. From the slopes, $\Delta\bar{H}_A$ values can be obtained, eq. (3). As is seen, the partial molar enthalpy of dilution depends slightly on temperature. In Table II average values are collected. The average values were taken from data in the low-temperature region, i.e., below T_s . Above the separation temperature the accuracy of swelling measurements is not sufficient to obtain reliably smooth curves, especially for nitrobenzene systems. Most probably it is due to the lower boiling point of the solvent.

From Table II it is seen that $\Delta\bar{H}_A$ values for MOCA-extended polyurethanes are relatively stable if compared with the values for BDO-extended polymers. In our opinion the data may be related to the perfection of microphase separation. One can expect the partial molar enthalpy of dilution of a solvent to be unchanged if the perfection of the separation is not altered. Thus, from the enthalpy considerations one may conclude that the completeness of the separation in BDO-extended polyurethanes is affected quite remarkably by changes in the amount

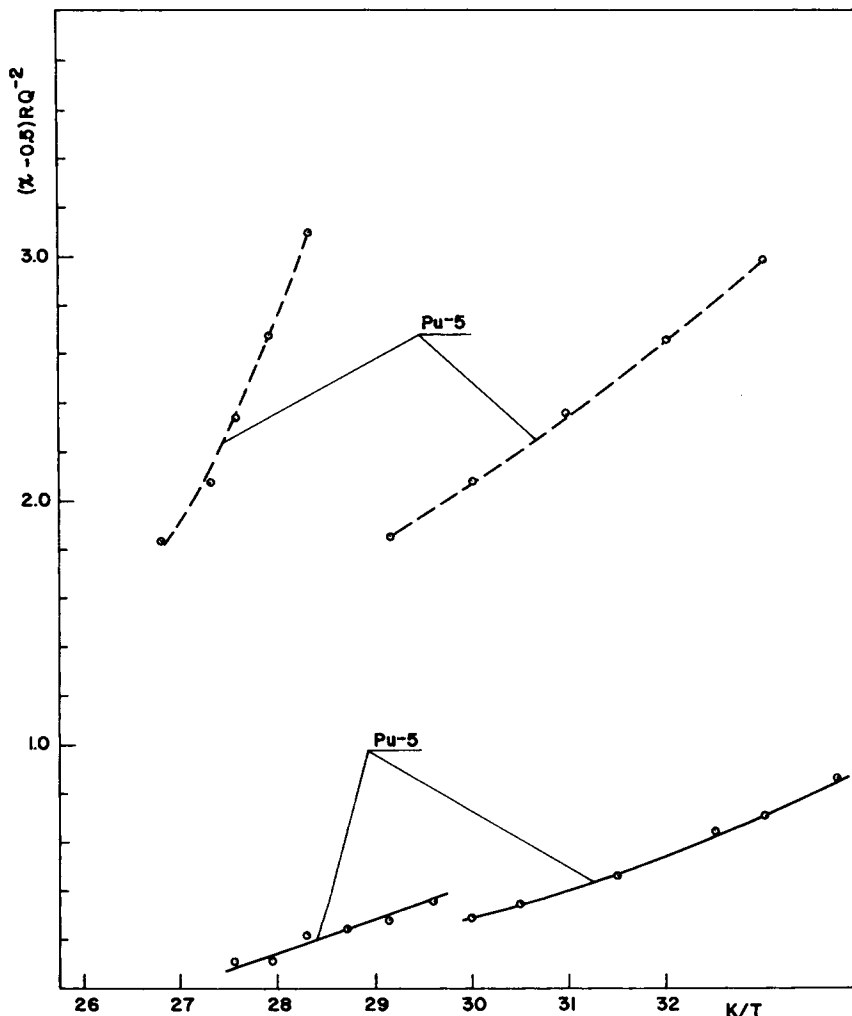


Fig. 7. Plot of $Rq^{-2}(\chi - 0.5)$ vs. $1/T$ for selected polymer-solvent systems: (—) nitrobenzene; (---) dibutylphthalate.

of hard-segment material. For MOCA-based polymers such effects are less visible

Such a reasoning is reinforced by modulus-temperature behavior presented in Figures 4 and 5. Basic types of modulus-temperature curves for block polymers have been identified by Bonart, Morbitzer, and Rinke.¹⁰ Two-phase block copolymers generally exhibit the presence of distinct glass transition temperatures. Between the two temperatures a constant modulus plateau exists. The more complete the phase separation, the more temperature independent the modulus becomes. Inspection of Figures 4 and 5 reveals that the temperature dependence of the modulus is essentially unchanged by variations in the weight fraction of hard segments as far as MOCA-extended polyurethanes are concerned. For BDO-based elastomers the flatness of the plateau is being diminished when the weight fraction of hard segments is increased. In the light of what has been quoted above about the correlation between phase separation and temperature

dependence of modulus, one can conclude from Figures 4 and 5 that the perfection of phase separation becomes poorer for BDO-based polymers if the weight fraction of hard segments is increased. For MOCA polyurethanes the perfection is not affected by the weight fraction in the investigated range. The conclusions are basically in line with those drawn from the swelling data. A note concerning Pu-5 should be added here. The modulus falls off at a considerably lower temperature. To the rapid decrease of the modulus may also contribute phase separation during preparation of the sample. Such separation is possible for higher BDO contents. Repeated preparations of Pu-5 had negligible effect on the results.

As previously mentioned, calculations of crosslinking density for the investigated systems may lead to doubtful results. To illustrate this, the effective number of network chains per unit volume, n , was calculated using Flory's formula¹:

$$\ln(1 - q^{-1}) + q^{-1} + \chi q^{-2} = -nV_A^0(q^{-1/3} - 0.5q^{-1}) \quad (4)$$

where V_A^0 denotes the molar volume of the solvent. The obtained results are rather peculiar. For example, for MOCA-based elastomers at 310 K, n increases with w_h from 0.002 to 0.006 mole/cm³ in nitrobenzene and from 0.02 to 0.120 mole/cm³ in dibutylphthalate. Similar trends are observed in BDO-extended elastomers. From the preparation scheme used in this work, one should not expect the crosslinking density to change essentially within the set of investigated samples since all the prepolymers were reacted with almost the same molar deficiency of the chain extenders. In fact, the quoted n values reflect more the extent of heterophase structure of the swollen samples than the crosslinking density. Following this reasoning, we tried to calculate n values well above the separation temperature. Unfortunately, the results were too scattered to draw any firm conclusions. The logarithmic term in eq. (4) requires precise values of q ; and in the high-temperature region swelling degrees by the method employed in this work are not accurate enough, the more so as the crosslinking density due to allophanate or biuret groups is small as a consequence of the molar compositions used in the preparation.

The domain structure of block copolymers, among them polyurethanes, has been drawing much attention. Mostly, quite sophisticated instrumental techniques are involved in the research. It seemed therefore worthwhile to us to show that the type of structure leaves its mark also on swelling properties and that even such an old-fashioned technique as swelling measurement may yield some information on the perfection of microphase separation.

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