THERMODYNAMICS OF SWELLING OF CROSS-LINKED POLYURETHANES

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THERMODYNAMICS OF SWELLING OF CROSS-LINKED POLYURETHANES

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Cross-linked polymers are acquiring ever greater importance in practice (binders, ion-exchange resin matrices, etc.). Therefore, the study of their properties and structure is urgently necessary. Valuable information on chain flexibility and packing density for linear polymers has been obtained from thermodynamic investigations of their dissolution processes. The thermodynamics of swelling of cross-linked polymers has so far been developed only in the direction of testing the applicability of the Flory–Rehner theory. Experimental data on the free energy, enthalpy, and entropy of swelling of networks are practically absent. The present work is the first attempt to carry out investigations of this kind.

Polyurethanes were chosen as the objects of study; their degree of cross-linking was chemically specified during synthesis by changing the concentration of trimethylolpropane C_T and was calculated from the formula $\nu/V = 3/2C_T$, where ν/V is the number of moles of chain segments between junctions per unit volume. By changing the ratio of triol and diethylene glycol taken for the synthesis, polyurethanes of different degrees of cross-linking were obtained at the same concentration of urethane groups. The starting products were carefully redistilled and recrystallized (^{1}).

All the polyurethanes whose characteristics are given in Table 1, after vulcanization, were elastomers and had an amorphous structure. During storage, samples of series B and G hardened and became cloudy, which was accompanied by the appearance of crystalline interferences in their X-ray diffraction patterns. The density* of the crystalline samples was higher than that of the amorphous ones (Table 1). As the degree of cross-linking increased, the density of the former decreased to the density value of the latter. This indicates that an increase in the frequency of the spatial network impedes crystallization.

The interaction of polyurethane with dioxane—a weakly polar liquid in which the amorphous polyurethanes studied dissolved or swelled athermally—was investigated. Before the beginning of the study, all samples of cross-linked structure were extracted with boiling dioxane to remove soluble fractions, while the linear products were reprecipitated from dioxane solutions with pentane. The samples were repeatedly washed with pentane and dried to constant weight at a residual pressure of 10^{-5} mm Hg.

Sorption was studied by the gravimetric method (^{2}) at a residual pressure of 10^{-5} mm Hg and $T = 20^\circ$. Tungsten spirals with a sensitivity of 6 mg/mm were used.

Figure 1 presents the sorption isotherms of dioxane on samples of series A, B, and V. It is seen that over a wide range of relative vapor pressures (up to $p_1/p_1^0 = 0.95$) the sorption capacity of polyurethane of a given chemical nature does not depend on the degree of cross-linking. Differences appear only near $p_1/p_1^0 \to 1$, and the equilibrium maximum degrees of swelling (ω_1), whose values are given in Table 1, with increasing–

* The density was determined by hydrostatic weighing on an analytical balance.

Table 1

Characteristics of the properties of polyurethanes

Conditional designation	Degree of crosslinking, $\nu/V \cdot 10^4$ mol/cm^3	M_c	ω_1	Density, g/cm^3: amorphous	Density, g/cm^3: crystalline	Integral heat ΔH, J/g: amorphous	Integral heat ΔH, J/g: crystalline	Heat of crystallization ΔH, J/g
-1	linear, mol. wt. 30,000			1.297		–0.10		
-2	0.5	27,700	–	1.297		–0.57		
-3	1.4	9,100	0.89	1.298		–0.58		
-4	2.5	5,200	0.87	1.296				
-5	2.9	4,500	0.78	1.297				
-6	4.3	3,000	0.71	–				
-7	5.7	2,300	0.70	1.297		–0.68		
-1	linear, mol. wt. 30,000			1.238		–2.42		
-2	0.5	24,700	–	–				
-3	1.1	11,500	0.90	1.238				
-4	1.5	8,200	0.84	1.238				
-5	1.8	7,000	0.81	1.237				
-6	2.1	5,800	0.81	1.237		–2.42		
-7	3.1	4,000	0.76	1.237		–2.66		
-8	6.2	2,000	0.71	1.237		–2.63		

Conditional designation	Degree of crosslinking, $\nu/V \cdot 10^4$ mol/cm^3	M_c	ω_1	Density, g/cm^3: amorphous	Density, g/cm^3: crystalline	Integral heat ΔH, J/g: amorphous	Integral heat ΔH, J/g: crystalline	Heat of crystallization ΔH, J/g
-1	linear, mol. wt. 30,000			1.154	1.182	-0.10	34.7	34.8
-2	0.4	27,000	0.90	1.154	1.178			(8.3 kcal/g)
-3	1.3	9,100	0.85	1.155	1.175	-0.10		
-4	2.5	4,500	0.79	1.154	1.157			
-5	5.1	2,200	0.72	1.155	1.156	0		
-1	linear, mol. wt. 20,000			1.185	1.218	–	39.30	
-2	2.6	7,200	0.80	1.187	1.207	–	29.50	
-3	5.6	3,300	0.76	1.188	1.205	-3.47	21.30	24.7
-3	5.6	3,300	0.76	1.188	1.205	-3.47	21.30	(5.9 kcal/g)

Note. Series A—polyethylene succinate urethane; series —polyethylene adipinate urethane; series —polyethylene sebacinate urethane; series —polybutylene adipinate urethane.

with increasing degree of crosslinking decrease regularly. The sorption capacity likewise does not depend on the phase state of the polyurethane: the experimental points for the crystalline and amorphized modification of samples B lie on one curve. The sorption capacity changes with the chemical nature of the polyurethane, increasing with an increase in the number of methylene groups between the ester bonds.

From the equations

$$\Delta\mu_1 = RT \ln \frac{p_1}{p_1^0}, \qquad \Delta\mu_2 = \int_a^b \frac{\omega_1}{\omega_2}\, d(\Delta\mu_1) \quad \text{and} \quad \Delta G = \omega_1 \Delta\mu_1 + \omega_2 \Delta\mu_2$$

$\Delta\mu_1$, $\Delta\mu_2$, and ΔG were calculated. The results obtained indicate that the thermodynamic affinity of dioxane for polyurethanes depends on their chemical nature and does not depend on the degree of crosslinking or crystallinity.

Fig. 1. Sorption isotherms

Figure 1: Fig. 1. Sorption isotherms

Fig. 1. Sorption isotherms:
a —polyurethane succinates: 1 —A-1, 2 —A-2, 3 —A-3, 6 —A-6, 7 —A-7;
b —polyurethane adipates: 1 —B-1, 2 —B-2, 5 —B-5, 6 —B-6, 7 —B-7, 8 —B-8;
c —polyurethane sebacinates: 1 —V-1, 2 —V-2, 3 —V-3, 4 —V-4, 5 —V-5.

The latter is reflected in the values of the integral heats of dissolution and swelling, which were determined calorimetrically (3). It follows from Table 1 that crystalline linear polyurethanes dissolve, whereas partially crystallized network samples swell with a rather strong absorption of heat; dissolution and swelling of their amorphized modifications are accompanied by a slight evolution of heat. The difference between these quantities is the heats of crystallization of the polyurethanes, which in order of magnitude are close to the heats of fusion of polyamides (4) and decrease with increasing degree of crosslinking.

Figure 2 gives the concentration dependence of the integral heats of dissolution and swelling of amorphous linear and network polyurethanes, obtained by the method described earlier (5, 6). Linear polyethylene succinate- and polydiethylene sebacinate urethanes dissolve, whereas network polyurethanes of any degree of crosslinking swell in dioxane athermally. Polydiethylene adipinate urethanes interact with dioxane with a small evolution of heat, the smaller the higher the network frequency.

For the curves in Fig. 2, by the method of intercepts, the partial enthalpies of mixing ΔH_1 and ΔH_2 were calculated; using these, from the equations

$$T\Delta S_1 = \Delta H_1 - \Delta\mu_1; \qquad T\Delta S = \Delta H - \Delta G,$$

the total and partial entropies of mixing of linear and network amorphous polyurethanes were computed; their concentration dependence is presented in Fig. 3.

On the basis of the data in Fig. 3 it may be concluded that, as the number of methylene groups between the ester bonds increases, the flexibility of the polyurethane chain increases, which agrees with the regularities found for polyamides (4). This is also indicated by the values of the thermodynamic segments (6, 7) M_2^*, which for polydiethylene succinate

are equal to 600, for polydiethylene adipate—400, and for polydiethylene sebacate—300. These values are smaller than the dimensions of the thermodynamic segments of polyisobutylene (^{2}), polyethylene, polypropylene, and polybutylene (^{8}), and indicate the high flexibility of the chains of these polyurethanes, caused by the presence of very flexible C—O—C bonds (^{9}).

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Fig. 2. Dependence of the enthalpy of mixing of polyurethanes in dioxane on concentration

Fig. 3. Dependence of the entropy of mixing on the composition of the solution: 1—polyurethane succinate, 2—polyurethane adipate (B-1), 3—polyurethane sebacate

The small value of the thermodynamic segment makes understandable the independence of all thermodynamic parameters of amorphous polyurethanes from the crosslinking frequency. At the maximum degree of crosslinking, the molecular weight of the segment between network junctions is $M_c = 2300$, which is considerably greater than the size of the thermodynamic segment; i.e., the crosslinking frequency does not affect the flexibility of the chain or the packing density of amorphous polyurethanes, as is evidenced by the unchanged density values (Table 1). A decrease in the degree of crosslinking has a substantial effect on the ability of polyurethanes to crystallize and orient both during storage and during stretching, which substantially changes their mechanical properties (1).

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Note: Figure translations are in progress. See original paper for figures.