Sov. J. Chem. Phys., Volume 2(12), 1985, pp. 2797–2803
0733-2831/85/0212-2797$20.00/0

Deviations from Equilibrium Dimerization of Carboxylic Acids in Polymer Matrix

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(Received November 29, 1982)

Studies of equilibria involving the formation and rupture of intermolecular H-bonds in the gas phase or in liquid solvents are usually performed with characteristic experiment times far exceeding H-bond system relaxation times which, according to the few data available, range from 10^{-10} to 10^{-4} s for various systems studied [1] to [4]. In particular, equilibrium is established in H-bond systems at each instant during sample temperature variations. Deviations from the regular dependence of the number of H-bonds on temperature (from the Van't Hoff law) were, however, observed in some low-molecular-weight substances ([5] to [7]) and polymers ([8] to [10]) at glass transition temperatures. The growth of that number with cooling slowed down, and at $T < T_v$ the number of free and H-bonded groups was independent of temperature, the degree of association remaining at the level reached at $T \cong T_v$. This was explained ([6], [8] and [10]) by the formation of a rigid molecular frame, where the mobilities of the molecules or polymer chain segments constituting the frame were substantially restricted.

The authors of Ref. [8] noticed a significant difference in the behavior of the H-bonds formed by carboxyl groups incorporated in side chains of a polymer and those of low-molecular-weight acids dissolved in a polymer. While for the former the equilibrium between free and H-bonded groups is froze near the glass transition point, the latter exhibit no such anomaly, and for them the monomer-dimer equilibrium continued to shift to the side of the dimer and followed the Van't Hoff law down to temperatures 60 to 80 K below T_v. The purpose of this work was to study the effects of polymer media, as solvents, on equilibria involving the formation and rupture of H-bonds. We checked the applicability of the Van't Hoff law in a wide temperature range below the glass transition point and studied the effect of the properties of the polymer matrix and of the associating low-molecular-weight species dissolved in it on deviations from this law.

EXPERIMENTAL

Solutions of aliphatic carboxylic acids in polystyrene (PS) and poly-α-methylstyrene (PMS) were studied in the range of 90 to 450 K by measuring their IR spectra. The acids were propionic, C_2H_5COOH (PA), trimethylacetic, $(CH_3)_3CCOOH$ (TA), and adamantanecarboxylic, $C_{10}H_{15}COOH$ (AA), acids; they have close monomer-dimer equilibrium parameters [11], but differ substantially in the size of the hydrocarbon radical. PS and PMS have analogous chemical structures and are very much alike as to the type of intermolecular interactions with substances dissolved in them. On the other hand, they have different glass transition temperatures (370 and 430 K, respectively).

Reprecipitated atactic polymers with molecular masses of 10^5 to 10^6 were used. Films, 50 to 200 μm thick, were prepared by casting from solutions in chloroform containing a weighted amount of an acid, and dried under vacuum. The acid concentrations in the films were 0.5 to 3.0 mass %. The samples were annealed at a temperature above T_v. The spectra were recorded on an UR-20 instrument. The polymer films were placed into cells equipped with electric heaters between rock salt windows and thin (6 μm) Teflon pieces. The spectra were taken in the range of 90 to 300 K using the type of cell-cryostat described in Ref. [12]. The film thickness was controlled with the help of a Teflon limiting ring. The samples were heated and cooled at a rate of 1 deg/min. The temperature was measured with an accuracy of 1 to 2° using a thermocouple. A reference beam was passed through a PS or PMS film. The equality of sample and reference film thicknesses was checked by comparing the intensities of the characteristic benzene ring bands at 1800 to 2000 cm^{-1}.

DISCUSSION

The carboxylic acids PA, TA, and AA undergo association to cyclic dimers containing two C═O...HO H-bonds. In the region of ν(C═O), the spectra of acids in polymer matrices exhibit two bands arising from monomer (1740 to 1750 cm^{-1}) and dimer (1700 to 1710 cm^{-1}) species, whose relative intensities depend on temperature and concentration. By way of example, see the spectra of AA in PMS taken at 20, 70, and 150°C (Fig. 1). The data obtained show that in the range of 450 to 370 K, temperature variations of the monomer-dimer equilibria are similar to those observed in liquid low-molecular-weight solvents: the Van't Hoff law is obeyed, the dimerization enthalpies and entropies have values similar to those found in solutions in toluene, a low-molecular-weight analog of polystyrene. Further cooling is accompanied by a slower variation of band intensities, which cease to change below 280 to 290 K. Freezing of the monomer-dimer equilibria thus becomes manifest in the temperature range 50 to 80 K below the polymer glass transition point. Other systems studied follow the same pattern.

Measurement of the acid monomer and dimer ν(C═O) band intensities can be employed to determine the fractions of monomer, α, and dimer, 1-α, species:

$$\alpha = [1 + (\varepsilon_m D_d/\varepsilon_d D_m)]^{-1},$$

where ε_m and ε_d are the absorption coefficients at the band maxima, and D_m and D_d are the optical densities of the monomer and dimer bands, respectively [8]. The dimerization reaction equilibrium constant is calculated from the equation

$$K = c_d/c_m^2 = (1-\alpha)/2\alpha^2 c,$$

where c is the acid concentration in the polymer matrix. For aliphatic

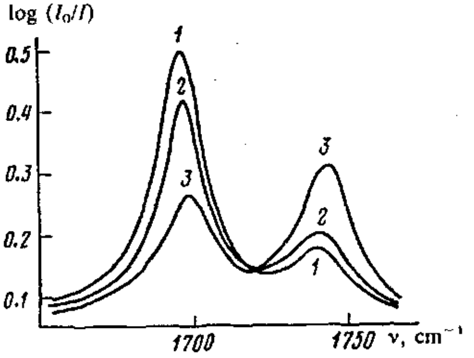

FIGURE 1 Absorption spectra of a poly-α-methylstyrene film containing adamantanecarboxylic acid at 20 (*1*), 70 (*2*), and 150°C (*3*).

carboxylic acids, $\varepsilon_m/\varepsilon_d \cong 0.7$. Since the acid concentration may decrease during the drying of the films under vacuum, we calculated the $(1-\alpha)/\alpha^2$ values proportional to the equilibrium constants.

The $\ln[(1-\alpha)/\alpha^2]$ vs. reciprocal temperature dependences are shown in Fig. 2. At high temperatures, these dependences are approximated by straight lines in agreement with the Van't Hoff equation. The straight line slopes are determined by the dimerization enthalpies, ΔH, which are 8 to 9 kcal/mol for the systems studied (to within 1 kcal/mol) and do not differ from the dimerization enthalpies found for aliphatic acids in liquid aromatic solvents. At lower temperatures, the $\ln[(1-\alpha)/\alpha^2]$ vs. T^{-1} dependences (Fig. 2) deviate from the straight lines, which means a departure from the thermodynamic equilibrium between free acid molecules and acid dimers. States corresponding to higher temperatures, i.e. with large numbers of monomer molecules, then become stabilized.

A comparison of the results obtained for various acids in PS and PMS matrices shows that the temperature range where the system passes from equilibrium to complete freezing of the monomer-dimer equilibrium in PS is several tens of degrees lower than in PMS. It is only natural to explain this observation by the structure and relaxation characteristics of the polymer matrices. It should first be mentioned that according to Refs. [8] and [9], where monomer-dimer equilibrium freezing was observed for acid copolymers with styrene near the glass transition temperatures (see curve *5* in Fig. 2

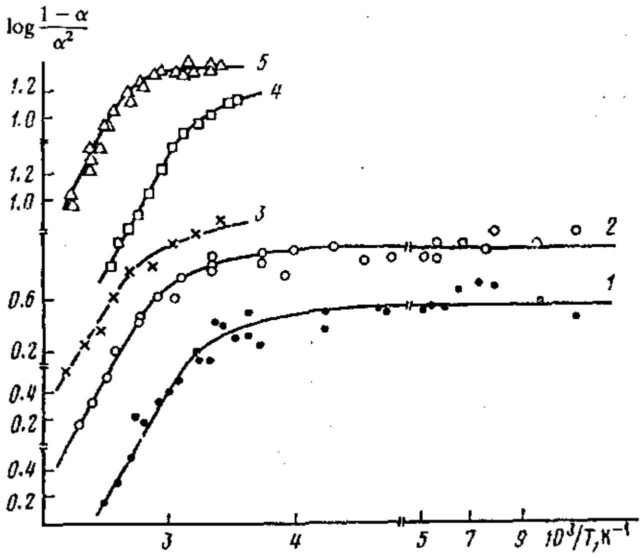

FIGURE 2 The $\ln[(1-\alpha)/\alpha^2]$ vs. $1/T$ dependences for propionic (*1*), trimethylacetic (*2*), adamantanecarboxylic (*3*, *4*) acids in poly-α-methylstyrene (*1* to *3*) and polystyrene (*4*) matrices, and for a copolymer of acrylic acid and styrene (*5*).

borrowed from Ref. [8]), the molecular process controlling the formation and dissociation of H-bonds consists in the segmental motions of macromolecules. Translational and rotational diffusion of low-molecular-weight species dissolved in polymers is, apparently, controlled by smaller-scale motions of parts of macromolecules.

Alongside the relaxation transition related to segmental mobility of macromolecules (α-transition), other transitions occurring at lower temperatures and related to the motions of small polymer chain fragments (β-transition) and side radicals (γ-transition and other transitions) were observed in many polymers. In particular, the β-transition in polystyrene occurs 40 to 50° below T_v [13]. Since this is just the temperature region where deviations from monomer-dimer equilibria become detectable, the conclusion can be drawn that freezing of smaller-scale chain motions corresponding to that transition has a substantial effect on the diffusion of low-molecular-weight substances dissolved in the polymer.

Figure 2 demonstrates three acids with very close thermodynamic dimerization parameters to show deviations from equilibrium at different temperatures increasing over the series PA, TA, and AA. Deviations from equilibrium thus depend on the size of molecules undergoing association and occur at higher temperatures for larger molecules. The most probable reason for that is the dependence of the monomer diffusion coefficient in the polymer solvent on the monomer size, shape, and degree of branching.

It should be borne in mind that the type of deviation from equilibrium depends on sample pretreatment and the mode of cooling. Quenching films annealed at a temperature above the β-transition point in liquid nitrogen yields a far larger number of frozen monomer molecules than with films cooled slowly.

The study of nonequilibrium states in systems of H-bonds in polymers can prove useful for elucidating the effects of the properties and molecular dynamics of a polymer matrix on the mechanisms and kinetics of chemical reactions. This subject has received much attention during recent years, for it pertains to the problem of stabilizing polymers [14]. Reactions with the formation of H-bonds can serve as convenient models in these studies because of their reversibility, nonactivation nature (in the gas phase), and the possibility of wide reaction parameter variations by varying the reagents.

The authors are thankful to A. F. Podol'skiĭ for providing poly-α-methylstyrene and to L. L. Kimtys for providing adamantanecarboxylic acid.

References

1. N. S. Golubev and G. S. Denisov, *Dokl. Akad. Nauk SSSR* 258, No. 5: 1142 (1981) (in Russian).
2. I. P. Gragerov, V. K. Pogorelyi, and I. F. Franchuk, *Vodorodnaya svyaz' i bystryi protonnyi obmen* (Hydrogen bond and fast proton exchange) (Kiev: Naukova dumka, 1978) (in Russian).
3. G. S. Denisov, S. F. Bureiko, N. S. Golubev, and K. G. Tokhadze, *Molek. Interac.*, Vol. 2, ed. H. Ratajczak and W. J. Orville-Thomas, 1981: 107.
4. K. G. Tokhadze, in: *Molekulyarnaya spektroskopiya* (Molecular spectroscopy) (Leningrad: LGU, 1975), vyp. 3: 81 (in Russian).
5. P. P. Kobeko, *Amorfnye veshchestva* (Amorphous substances) (Leningrad: Izd. Akad. Nauk SSSR, 1952) (in Russian).
6. S. N. Zhurkov and B. Ya. Levin, *Dokl. Akad. Nauk SSSR* 72, No. 2: 269 (1950) (in Russian).
7. A. Barkatt and C. A. Angell, *J. Chem. Phys.* 70, No. 2: 901 (1979).

8. A. G. Zak, N. A. Kuznetsov, I. S. Lishanskiĭ, and A. L. Smolyanskiĭ, *Izv. Vuzov. Khimiya i Khim. Tekhnologiya* 18, No. 6: 951 (1975) (in Russian).
9. Y. Kihira, *J. Sci. Hiroshima Univ., Ser. A* 40, No. 2: 293 (1976).
10. S. N. Zhurkov and B. Ya. Levin, *Dokl. Akad. Nauk SSSR* 67, No. 1: 89 (1949) (in Russian).
11. L. Kimtys and V. Balevicius, *Adv. Molec. Relaxation Interact. Proc.* 15, No. 2: 151 (1979).
12. G. S. Denisov, A. I. Kul'bida, Z. Z. Rechapov *et al.*, *Khim. Fiz.*, No. 2: 221 (1982) (in Russian).
13. V. A. Bershtein, V. M. Egorov, L. G. Razgulyaeva, and V. A. Stepanov, *Vysokomolek. Soed.* A20, No. 10: 2238 (1978) (in Russian).
14. N. M. Emmanuel', *Vysokomolek. Soed.* A21, No. 11: 2624 (1979) (in Russian).