хим. физ. 1982, 1(2), с.221-6

Sov. J. Chem. Phys., 1982, Number 2, pp. 403-412
0733-2831/83/8202-0403$25.00/0

The Effect of Molecular Mobility of the Medium on Proton Exchange in Polymer Films. The System Styrene Copolymer with Methacrylic Acid – Amine

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IR spectra were recorded for films of styrene copolymer with methacrylic acid, with additions of aliphatic amines, in the temperature range from -190 to 120 °C. The amines were shown to form complexes with acid residues in the copolymer. In the case of tertiary amines, these are complexes with hydrogen bonding of the type $O{-}H\ldots N$; secondary amines are characterized by the equilibrium $O{-}H\ldots \rightleftarrows O^-\ldots H{-}N^+$ caused by proton exchange. At $t > {\sim}40^\circ C$, the equilibrium shifts towards the ionic form of the complex with a decrease in temperature; at $t < {\sim}40^\circ C$, the equilibrium appears to be frozen: it remains unchanged when temperature is lowered to -190 °C. Therefore, proton exchange becomes impossible due to the stability of the medium. The results are compared with the known facts of β-transition found in polystyrene and its copolymers at 40 to 60 °C. The authors discuss the scale of molecular mobility required for proton exchange in a complex with hydrogen bonding.

(Received September 30, 1981)

The mobility of molecules in the medium plays a significant role in the mechanism of many elementary processes occurring in the condensed phase [1]. The statement appears to hold not only for bimolecular reactions whose kinetics is controlled by diffusion, but also for many intromolecular and intracomplex reactions. The latter include a reversible proton exchange in complexes with hydrogen bonding

$$AH\ldots B \rightleftarrows A^-\ldots HB^+, \qquad (I)$$

where $AH\ldots B$ is a molecular complex and $A^-\ldots HB^+$ is a nondissociated ionic pair. The equilibrium of type (I) occurs in complexes formed by amines with many strong proton donors (phenols, carboxylic acids, etc.) in various, including nonpolar, solvents (see review [2]). In all the systems studied, the equilibrium shifts toward the ionic form with a decrease in temperature [2-6]. However, as was found in [7] when examining UV spectra for complex of chlorophenols with amines at low temperatures, a shift of the equilibrium and the corresponding redistribution of band intensities cease upon solvent transition to the glassy state, i.e., the equilibrium is "frozen". Therefore, a proton exchange is accompanied with such a rearrangement of the complex and the solvate envelope surrounding it, which is impossible in a rigid glassy medium.

It would be of interest to study the temperature dependence of equilibria similar to (I) in amorphous polymers in which the glass transition temperature corresponds to mobility freezing for large segments containing $\sim 10^2$ monomeric units in the main chain (α-transition) [8,9]. Below this temperature, some smaller scale mobilities remain in the polymer, but these also freeze gradually with a decrease in temperature. Examining the equilibrium (I) under these conditions would make it possible to estimate the scale of mobility which is required for proton exchange.

EXPERIMENTAL

Experiments were conducted with films of a styrene copolymer with methacrylic acid containing an additive of molecular low weight aliphatic amine. As was shown in [10], interaction of amines with acid units of such copolymers in solutions occasionally results in equilibrium (I) which distinctly manifests itself in IR spectra.

The samples with a molecular mass of $\sim 2 \cdot 10^5$ contained 3.5% of acid units. Films were prepared by splashing of a solution containing the copolymer and the amine in $CHCl_3$ on the surface of a window made of CaF_2 or KBr. The amine concentration was usually 3-4 times as high as that of the acid units in order to suppress their dimerization and the formation of acid-amine complexes having a composition of 2:1. IR spectra were recorded with an UR-20 spectrophotometer. A cuvette-cryostat fitted with an electric heater made it possible to perform measurements within the range of 80 to 450 K. A film 70-100 μm thick with a Teflon filler fixing the layer thickness was clamped between two windows and put into a massive copper holder attached to the inner casing of the cryostat. Indium fillers were used to improve heat contact between the windows, the holder, and the casing. Films were annealed and solvent traces were removed in the evacuated cyrostat. The temperature was measured with an accuracy of ~1° using a copper-constantan thermocouple. A polystyrene film with an adjusted thickness was placed in the reference cell of the spectrophotometer in order to compensate absorption bands of styrene units. To find the temperature range of glass transition for studied samples, curves for their specific heat as a function of temperature were obtained with a Termophlex calorimeter[1].

RESULTS AND DISCUSSION

In the absence of the amine, the IR spectra of the films show bands at 1745 and 1700 cm^{-1} induced by the vibrations $\nu(C=0)$ of free and dimerized carboxy groups (Fig. 1, curve 1). The relative intensities of the bands depend on the concentration of acid units in the copolymer and, at a temperature higher than that of its glass transition, also on temperature [11]. Specific heat measurements have shown that glass transition occurs in the samples within the temperature range of 75 to 100°C. At a lower temperature, the ratio between the concentrations of free and dimerized acid units does not depend on temperature. Hence, hydrogen bonds between the acid units can be formed or cleaved only if the segments of the macromolecular chain retain their mobility.

If the films are prepared with an additive of teriary amines (tributylamine, trioctylamine), only a band at 1700 cm^{-1} is present in this region of their IR spectra (Fig. 1, curve 2). It coincides in its position with the band for the acid dimer, but is much wider. Consequently, just as in solutions [10], it belongs to the vibration $\nu(C=0)$ of the complex acid-amine of the molecular type

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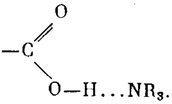
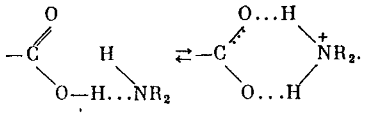
[1] The authors are indebted to G. A. Tsereteli for conducting the measurements.



Such a band is present also in IR spectra for complexes of tertiary amines with acids similar in their proton-donor activity to methacrylic acid (acetic and isobutyric acid) dissolved in low-molecular-weight nonpolar solvents [2-4]. However, according to [4,12], these complexes are characterized by the equilibrium (1). It is shifted far toward the molecular form at room temperature but, as the temperature decreases, the concentration of ionic pairs rises rapidly and the corresponding bands appear in the spectra. No bands that could be assigned to complexes of the ionic type have been detected in the spectra of the films in the presence of tertiary amines either at room temperature or at far lower temperatures down to 80 K.

If a secondary amine is added to the film, the IR spectrum has not only a band at 1710 cm^{-1} associated with the vibration ν (C = 0) exhibited by the complex acid-amine of the molecular type, but also bands at 1560 and 1630 cm^{-1} characteristic of the vibrations $\nu_a(CO_2^-)$ of the carboxylate anion and $\delta(NH_2^+)$ of the dialkylammonium cation, respectively (Fig. 2). According to the data for solutions [3,4,10], this indicates that an equilibrium of the following type exists in the system:



(II)

In the series of dimethyl-, diisobutyl-, diethyl-, and dibutylamine, the intensity of the band at 1710 cm^{-1} falls while the intensity of the bands for the ionic form rises in accordance with the growth of the proton-acceptor activity of an amine. The spectra show also an intensive band at 1470 cm^{-1} and a weak band at 1690 cm^{-1} whose origin is obscure.

When the temperature dependence of the equilibrium (II) was studied, spectra were recorded at different temperatures both in the normal regime and in the differential one. In the latter case, identical films were put into the two cells of the spectrophotometer, and the temperature of the film was changed in the sample cell while it remained constant (28 °C) in the reference cell. The two types of spectra are shown in Fig. 2. One can see that the intensities of bands are noticeably redistributed only at $t > \sim 40$°C. Here, the intensity of the band at 1710 cm^{-1} increases with a rise in temperature, whereas that of the bands at 1560 and 1630 cm^{-1} falls. Therefore, just as in solutions, the equilibrium shifts toward the molecular form with an increase in temperature. This finding indicates that the reaction of proton exchange is exothermic. The intensity of the band at 1470 cm^{-1} changes similarly to that of the bands at 1630 and 1560 cm^{-1}; hence, this band should also be assigned to the ionic complex. The band at 1690 cm^{-1} does not undergo any noticeable changes with temperature (it is absent in the differential spectra) and, apparently, belongs to some vibration of the complex, which is only slightly susceptible to proton exchange.

Temperature decrease below 40°C causes minor, if any, changes in the spectrum. A fall of temperature to 80 K makes the bands somewhat narrower, slightly shifts their maxima, but the ratio between the band intensities for the molecular and ionic forms remains unchanged for all practical purposes.

The spectra were used to calculate the ratio between the concentrations of ionic pairs and molecular complexes (c_i/c_c) at different temperatures. To this end, the integral intensity D_k^0 of the band at 1710 cm^{-1} and the overall integral intensity D_i^0 of the bands at 1630, 1560, and 1470 cm^{-1} associated with the ionic form were found from the standard spectra at 28°C using graphic separation of the bands. The integral intensity of the band at a certain temperature T is

$$D(T) = D^0 + \Delta D(T).$$

where $\Delta D(T)$ is a value recorded in the differential spectrum at this temperature. If equilibrium (II) alone exists in the system then

$$\Delta D_i/A_i = -\Delta D_c/A_c,$$

where A_i and A_c are integral coefficients for the absorption of bands of ionic pairs and molecular complexes, respectively. The experimental dependence of ΔD_i on ΔD_c is a straight line. Therefore, the equilibrium (II) is unique, indeed, as has been supposed; moreover, A_i and A_c must either be independent of temperature or depend on it in a similar fashion. The slope of the line gives the value of A_c/A_i which was used to calculate c_i/c_c at each temperature

$$c_i/c_c = A_c(D_i^0 + \Delta D_i)/A_i(D_c^0 + \Delta D_c).$$

Figure 3 shows ln (c_i/c_c) as a function of 1/T. At $t > 60$ °C, the points fit in well with the line. This means that the system manages to follow temperature and is therefore in the state of thermodynamic equilibrium. In this temperature range, the c_i/c_c is the constant variation of equilibrium (II) and, for this region in Fig. 3, one can find a change in the enthalpy ΔH and a change in the entropy ΔS upon a proton exchange between the hydroxyl of the acid unit and the amine nitrogen. For dibutylamine, $\Delta H = -5.3 \pm 0.3$ kcal/mole and $\Delta S = -14.5 \pm 0.5$ cal/deg·mole. Similar values have been obtained for other secondary amines.

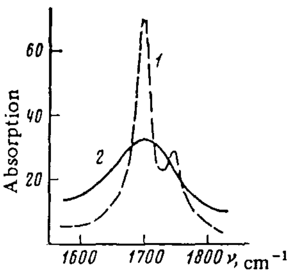


Fig. 1

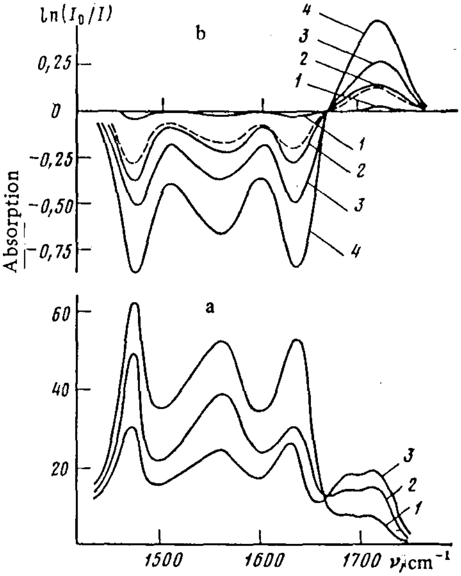


Fig. 2

FIGURE 1. Absorption spectra of the pure copolymer film (1) and the copolymer film containing an additive of trioctylamine (2).

FIGURE 2. Absorption spectra (*a*) of the copolymer films with additives of dibutylamine (1), diethylamine (2) and dimethylamine (3) at 28°C. Differential spectra (*b*) of the film with dibutylamine recorded when the non-annealed film (solid lines) was heated at 40°C (1), 60°C (2), 80°C (3) and 100°C (4) and then cooled (dashed line). The temperature of the sample in the reference cell was 28 °C.

At 60 to 40 °C, the dependence of $\ln(c_i/c_c)$ on 1/T deviates from a linear one; at still lower temperatures, c_i/c_c does not change with temperature and remains constant within the experimental error. The specific value of c_i/c_c within this temperature range depends on the rate at which temperature changes and on the past history of the sample, which indicates that the relaxation time of the system is long. This can be seen in Fig. 3 where curve 1 corresponds to the temperature rise of the original non-annealed sample. When the temperature of this, now annealed, sample is decreased (and increased or decreased afterward), the points fall onto curve 2. The position of the inflection point also depends on the rate at which the temperature changes.

Therefore, the shift of the equilibrium between the molecular and ionic forms of the complex terminates at $t \sim 40$°C. It becomes clear why, in contrast to spectra for solutions of carboxylic acid complexes with tertiary amines, the spectra of films containing tertiary amines have no bands for the ionic form (see above). In these systems, at $t \sim 40$°C and above, the equilibrium is strongly shifted toward the molecular form, whereas, at lower temperatures, the rigidity of the medium does not permit the rearrangement of the complex required for proton exchange.

The question arises: why is the equilibrium frozen in the region of 40°C and what are the characteristics of molecular movement in a copolymer under these conditions? As was noted above, experiments were performed, as a rule, with samples in which the quantity of the added amine was ~3 times as large as that of the acid units. Calorimetric measurements have shown that the temperature range of glass transition shifts in such samples to 50–75°C (as compared with 75–100°C for films without the amine). Therefore, addition of the amine has a plasticizing action. It has been shown, however, that only free amine molecules are plasticizers since glass transition of samples within amine concentration equal to that of the acid units occurs, for all practical purposes, within the same temperature range as for a pure polymer. At such a concentration ratio, the film spectra contain also residual bands of free and dimerized acid units, and possibly, of acid-amine complexes of 2:1 composition. This makes the study of proton exchange in the 1:1 complex more difficult; here, too, however, any temperature-induced changes in the spectrum cease within the range of 30 to 40°C.

It can be concluded therefore that the equilibrium caused by proton exchange in complexes of amines with the acid units of a polymer is frozen below the temperature at which glass transition of the copolymer occurs, i.e., below the α-transition temperature. Therefore the data of [13–15] are of *interest: according to them, the so-called β-transition takes place in atactic polystyrene, as well as in certain copolymers prepared on its basis*, at $t \sim 40$°C. Although the mechanism of β-transition is still subject to debate and may be different in various polymers, most authors believe that, in the case of polystyrene, β-transition is induced by the freezing of the rotary movement of small (1–3 units) regions in a polymer chain [8,9]. One may presume therefore that the scale of molecular mobility and the value of the free volume required for proton exchange between the acid unit of the copolymer and the amine roughly correspond to those which are frozen in the temperature range for β-transition.

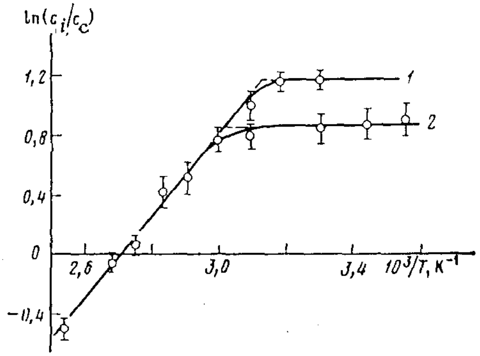


FIGURE 3. Logarithm of the ratio between the concentrations of ionic and molecular complexes as a function of 1/T for the copolymer film with a dibutylamine additive (1=heating of the non-annealed sample; 2=cooling).

Thus, analysis of the results suggests the following conclusions: the existence of certain mobility in the molecular surroundings is a prerequisite for proton exchange in complexes with hydrogen bonding; just as in low-molecular-weight solvents, there is a temperature region in polymeric media within which the scale of mobility is insufficient for proton exchange, and the equilibria induced by proton exchange are frozen; the boundary of this region in the system styrene copolymer with methacrylic acid-amine is in the vicinity of 40°C and apparently corresponds to the β-transition temperature.

The results of studies with ionomers prepared on the basis of styrene, which have been conducted in a series of works [16,17] using different techniques, show that intrachain association of ionic pairs is possible in such compounds and that ionic clusters are formed at a high concentration of the ionic component. In particular, for styrene copolymers with sodium methacrylate, an appreciable number of clusters appear at concentrations of the ionic units $\geqslant 6\%$. In the samples studied in the present work, the acid units amounted to 3.5% of the total unit number. Moreover, the data on the viscosity of such copolymers in solutions [10] indicate that the degree of association of ionic pairs containing alkylammonium cations is lower than for Li, Na and other cations. The equilibria studied here are observed, with the same spectroscopic characteristics, in highly diluted, low molecular weight solutions. It is possible that the effects found in this work are not directly related to the process of aggregation of ionic forms. No features of such an aggregation could be detected by spectroscopy. Other techniques, such as relaxation or X-ray analysis, should be used as well in order to finally solve this problem.

References

1. A. I. Burstein, *Uspekhi khimii* 47, No. 2: 212 (1978).
2. N. S. Golubev, G. S. Denisov, and V. M. Shraiber, in: *Vodorodnaya svyaz* (Hydrogen bonding) (Moscow: Nauka, 1981): 285.
3. G. V. Gusakova, G. S. Denisov, A. L. Smolyansky, and V. M. Shraiber, *Doklady AN SSSR* 193, No. 5: 1065 (1970).
4. G. V. Gusakova, G. S. Denisov, and A. L. Smolyansky, *Zhurnal Prikladn. Spektroscopii* 17, No. 4: 666 (1972).

5. G. S. Denisov and V. M. Shraiber, *Doklady AN SSSR* 215, No. 3: 841 (1974).
6. H. Baba, A. Matsujama, and J. Kokubun, *Sp. Acta* 25a, No. 10: 1709 (1969).
7. A. I. Kulbida and V. M. Shraiber, *Doklady AN SSSR* 250, No. 4: 889 (1980).
8. R. F. Boyer, *Polymer* 17, No. 11: 996 (1976).
9. G. M. Bartenev and Yu. V. Zelenev, *Kurs fiziki polimerov* (Physics of polymers. A. Manual) (Leningrad: Khimiya, 1976).
10. A. G. Zak, N. A. Kuznetsov, I. S. Lishansky, and others, *Vysokomolek. Soyedin.* A17, No. 2: 275 (1975).
11. A. G. Zak, N. A. Kuznetsov, I. S. Lishansky, and A. L. Smolyansky, *Izv. Vuzov. Khimiya i Khim. Tekhnolog.* 18: 951 (1975).
12. N. S. Golubev, G. S. Denisov, and A. I. Koltsov, *Doklady AN SSSR* 232, No. 4: 341 (1977).
13. O. Yano and Y. Wada, *J. Polymer Sci.* A-2, 9, No. 4: 669 (1971).
14. V. A. Berstein, V. M. Yegorov, L. G. Razgulyayeva, and V. A. Stepanov, *Vysokomolek. Soyedin.* A20, No. 10: 2278 (1978).
15. V. A. Berstein, M. Z. Petkevich, L. G. Razgulyayeva, and V. A. Stepanov, *Vysokomolek. Soyedin.* A20, No. 12: 2681 (1978).
16. A. Eisenberg and M. Navratil, *Macromolec.* 6, No. 4: 604 (1973); 7, No. 1: 84 (1974).
17. M. Hodge and A. Eisenberg, *Macromolec.* 11, No. 2: 283 (1978).