Sov. J. Chem. Phys., Vol. 6(2), 1990, pp.440–450
Photocopying permitted by license only

Printed in the United Kingdom

DEPARTURE FROM EQUILIBRIUM IN THE SYSTEM OF HYDROGEN BONDS IN POLYMERIC MATRICES

G.V. Gusakova, G.S. Denisov, Z.Z. Rechapov and A.L. Smolyanskii

Vologda Milk Institute, Vologda
Leningrad State University, Leningrad

The IR spectroscopy technique was used to study the regularities of the appearance of nonequilibrium states during the complex-formation process $AH+B \rightarrow AH...B$ in polymeric matrices - polystyrene and poly-α-methylstyrene. Pentafluorphenol was used as the proton donor esters as the proton acceptor. The approach consisted in testing the validity of van't Hoff's law with a temperature range covering the regions of relaxational transitions of the matrix. It is shown that the departure of the system of hydrogen bonds from the state of equilibrium occurs at a temperature corresponding to the β-relaxation transition of the polymer matrix. The magnitude of the temperature range for the transition of the hydrogen bonds from the equilibrium to the frozen state is different for active and passive matrices. The equilibrium in the hydrogen-bond system becomes completely frozen for the temperature region of the γ-relaxation of polystyrene and poly-α-methylstyrene.

(Received March 28, 1986)

The existence of nonequilibrium states below the glass transition temperature in hydrogen-bonded viscose media has been repeatedly recorded by spectral methods /1-4/. As a rule, deviation from the equilibrium distribution in a system of hydrogen bonds have been interpreted by the authors of the works cited on the basis of the concepts of a sharp decrease of the mobility of molecules or their fragments during the formation of rigid structure in the region of glass-transition temperature T_g. In investigations of specific features of behaviour of hydrogen bonds in polymer chains /5,6/ the authors have noted differences in the properties of active (if one of the partners is chemically linked to the polymer chain) and passice (if the low-molecular proton donor and acceptor are dissolved in the polymer) polymeric matrices. It has been found that the dimerization of carboxylic acids in the passive matrix is frozen in a temperature range corresponding to the β-transition in the polymer, i.e. 40-80° lower than T_g.

The present paper is concerned with the further study of the regularities of generation of nonequilibrium states in the course of the complex-formation process $Ah+B\rightarrow AH...B$ in the polymer matrices. The IR absorption spectra were used to study hydrogen-bonded complexes OH...O=C formed by pentafluorophenol (PFP) with esters. Just as in /5,6/ the approach used here consists of testing the validity of van't Hoff's law in a wide temperature range, including the regions characteristic relaxational transitions in polymeric matrices. The polymers used were polystyrene (PS) and poly-α-methylstyrene (PMS), which have a similar chemical structure but differ noticably in the glass-transition temperature (T_g=370 and 440 K, respectively), and also a statistical copolymer consisting of 3-10 mole.% methylmethacrylate and styrene (the copolymer MMA-St.).

Experimental

We used reprecipitated polymers and copolymers with a molecular mass of 10^5-10^6. Films of thickness 50-100 μm were prepared for solutions in chloroform containing a measured-out amount of PFP and ester and then dried in a vacuum until the ν_{CCl} band of chloroform disappeared into the IR spectrum. A stack consisting of a few such films was placed between flat quartz plates and pressed at $T > T_g$. A stopping ring of teflon 300 μm thick prevented the spread of polymer. The IR spectra were recorded on a UR-20 spectrophotometer. The work was carried out at the ν_{OH} band of PFP in the region of 3200-3600 cm^{-1}. The films were placed b-tween the rock salt windows in a holder equipped with an electric heater; for low temperature measurements they were placed in a cryostat cooled with liquid nitrogen. The temperature was measured with a copper-constant thermocouple to within 1-2°. To compensate for the self-absorption of the polymer matrix, a film containing no PFP was placed in the comparison channel of the spectrophotometer. The equality of the film thickness is both channels was monitored by measuring the intensity of the characteristic bands of the benzine rings in the range 1800-2000 cm^{-1}.

Results and Discussion

Pentafluorophenol-ester complexes in low-molecular solvents.

Pentafluorophenol (PFP) molecules, which display a relative strong proton-donor ability, are not liable to undergo self-association: in the spectra of solutions in CCl_4 of the concentrations below 0.5 mole/l there is observed a ν_{OH} band at the 3573 cm^{-1} of monomeric phenol and the intensity of the band of associates is low. Solutions of PFP in toluene, which may be regarded as a low-molecular analogue of PS and PMS, are characterized by the ν_{OH} band at 3502 cm^{-1} (Fig.1). The low-frequency shift of this band compared to the solution of the PFP in CCl_4 is due to the formation of a weak hydrogen bond $C_6F_5OH...\pi$-electrons of the toluene molecule. As can be seen from Fig.1, when ester is introduced into the PFP solution of toluene, a new ν_{OH} band appears in addition to the band at 3502 cm^{-1} in the spectra t 3280 cm^{-1}, which belongs to the compolexes $C_6F_5OH...O=C$. Its intensity decreases both upon thinning the solution and with increasing the temperature, and the intensity of the bands of the PFP-toluene complexes at 2502 cm^{-1} is enhanced. It is important to note that the intensity of the ν_{OH} band at 3573 cm^{-1} of free phenol is very low and, hence, in toluene solutions practically all of PFP is linked to the ester or solvent molecules.

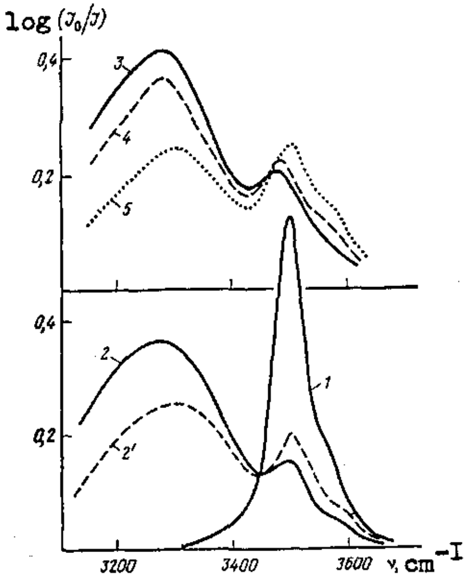

Fig. 1. Absorption spectra of the solution of PFP in toluene (1) in toluene in the presence of ethyl myristate (2, 2') and in a methylmethacrylate-styrene copolymer (3,4,5). The concentration is (mole/l) 0.2 PFP, 0.4 ethyl myristate (2), the temperature is 25(1,2), 72 (2'), 10 (3), 60 (4) 110°C (5).

The process of formation and breaking of the hydrogen bonds PFP with esters is characterized by the equilibrium constant

$$K=C^{A}{}_{B}/C^{A}C^{B}, \tag{1}$$

where C^A and C^B are the concentrations of PFP and ester molecules which are not bound to each other; C^{AB} is the concentration of the complexes. The value C^A was determined by measuring the optical density D at the maximum of the 3573 and 3502 cm^{-1} bands (solutions in CCl_4 and toluene, respectively), by using their absorption coefficients 505 and 330 l/mole., cm and the values of C^{AB} and C^B were found from the balance: $C^{AB}=C_0{}^A-C^A$, $C^B=C_0{}^B-C^{AB}$, where $C_0{}^A$ and $C_0{}^B$ are the initial concentrations of the PFP and ester. The values of the equilibrium constant K at 25° and of the ethalpy change ΔH upon formation of the PFP-ethyl myristate complexes found from the linear dependence of log K on 1/T appeared to be equal to 110 l/mole and 6.5±0.4 kcal/mole (CCl_4 solutions) and 15 l/mole and 5.2±0.3 kcal/mole (solutions in toluene). For the other esters we obtained close values of the thermodynamic characteristics of complexes. The value of ΔH in the case of boluene solutions are lower since this solvent PFP forms a hydrogen bond with the high-electrons of toluene /7/.

PFP-ester complexes in the passive polymer matrix. In studying the regularities of the formation of the hydrogen bonds in the passive polymer matrices of PS and PMS, PFP and the esters of mono- and dicarboxcylic acids were used as partners: myristic, $CH_3(CH_2)_{12}COOC_2H_5$; glutaric, $CH_3OOC(CH_2)_3COOCH_3$; sebacic, $C_4H_9OOC(CH_2)_8COOC_4H_9$. These esters have a low vapour pressure, which prevented their vaporization on vacuum drying of the polymeric films produces from solution.

In the ν_{OH} range the spectra of PS films with PFP and ester molecules introduced in them are analagous to the spectra of the solutions of these compounds in toluene. A lowering of the film temperature is accompanied by an increase in the intensity of the ν_{OH} band of the PDFP-ester complex and by a decrease in the intensity of 3480 cm^{-1} band of complexes PFP with the π-electrons of styrene units. However, below 320-300 K the effect of the temperature on the intensity of the ν_{OH} bands first becomes less noticable and then disappears altogether.

The specific features of the behaviour of the hydrogen bond system in the polymer matrix can be revealed by testing the validity of the vant Hoff law in a temperature range covering relaxation transitions in the polymer matrix /8/. Since the PFP and ester concentrations may vary during the preparation of films it is sufficient for the purposes of the present work to measure only the temperature dependence of the ratio C^{AB}/C^{A}, which is proportional to K with admissible accuracy. Indeed, as can be seen from Eq.(1), with the condition $C_0^B \geq 1.5 C_0^A$, $C^A \ll C_0^A$, which was fulfilled in all the experiments, the value of $C^B=C_0^B-C^{AB}=C_0^B 0 C_0^A+C^A$ varies with temperature within very narrow limits. Therefore, the temperature behaviour of the quantity log (D^{AB}/D^{A}) will be analagous to that of log K. Here D^{AB} and D^{A} are the optical densities for the ν_{OH} bands of PFP bound to the ester molecules and free under the assumption that the absorption coefficients for these bands are equally temperature independent.

Figure 2 presents the plots of log (D^{AB}/D^{A}) versus 1/T for the PFP-ester systems in PS and PMS matrices. At high temperatures ($T>320$ K for PS and $T>370$ K for PMS) these dependences are approximated by straight lines in accordance with the vant Hoff law. The resulting values of the enthalpy change for the formation of the complex $C_6F_5OH...O=C$ in the matrix are close to enthalpy of the hydrogen bond formed by the PFP with the same esters in toluene. As the temperature drops, there are deviations of the log (D^{AB}/D^{A}) versus 1/T plot for linearity, this being evidence of the upsetting of the thermodynamic equilibrium between the free molecules and the complexes. In this interval the states corresponding to higher temperatures, i.e. those with an increased number of free molecules, become stabilized. With $T<180$ K for PMS and 240 K for PS the quantity log (D^{AB}/D^{A}) is no longer temperature dependent, and equilibrium between the free and bound molecules is completely frozen.

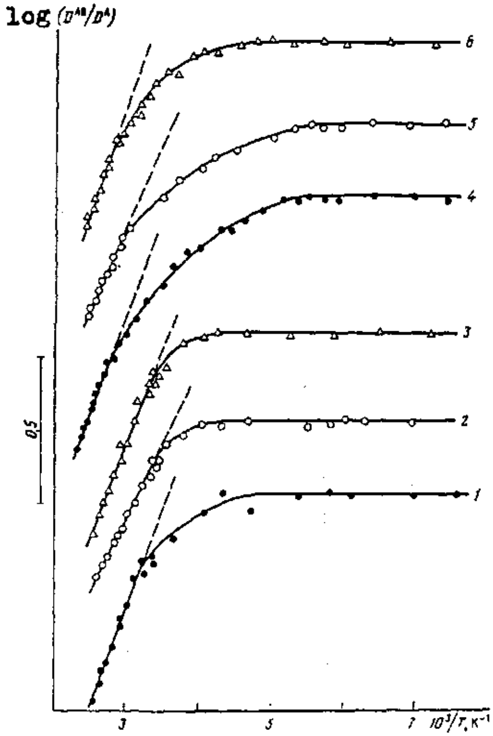

Fig. 2. Plot of the logarithm of the ratio of optical density of bound and free hydroxyl groups against 1/T for systems consisting of PFP and ethyl myristate (1,4), PFP and dimethylglutarate (2,5), and of PAFP and disobutylsebacate (3,6) in PS (1,2,3) and PMS (4,5,6) matrices.

A comparison of the results obtained for each of these complexes in PS and PMS matrices shows that in (1) the departure of the hydrogen bond system in the state of equilibrium occurs at temperatures dependent on the nature of the matrix; (2) these temperatures are 60-70° lower than the glass transition temperature

(3); transition of the hydrogen-bond system from the equilibrium to the frozen state takes place over a wide temperature range;(4) the temperature at which equilibrium for PS matrices becomes completely frozen in ~40° higher than in the case of PMS matrices.

In interpreting the results obtained on the basis of the concepts of relaxational processes in polymer matrices, it is essential to establish the scale of mobility of polymeric chains which limit the translational and rotational diffusion of the low-molecular compound dissolved in polymers which is responsible for the formation and breaking of hydrogen bonds. Since the disequilibrium of the process observed begins to manifest itself in polymers in the glassy state (at $T \approx T_g$-60) it becomes obvious that the formation of hydrogen bonds between small molecules is controlled not by the cooperative segmental motion of the polymeric chains, which become frozen upon α-transition, but by a smaller-scale motion. According to Bershtein and Yegorov /8/, the transition closest in temperature to α-transition (β-transition) lies 50-60° below T_g and is due to the noncooperative motion of the portions of macromolecular commensurate with Kuhn segment (8 monmeric units of PS and PMS). This transition is realized at sites of free-volume fluctuations, such sites in the polymeric matrix being primarily structural defects generated by small molecules incorporated in the matrix. The decrease in the diffusion coefficient of small molecules and the associated departures of the hydrogen-bond system from the equilibrium states occur presumably at temperatures corresponding to the point when the β-relaxation process, whose relaxation time spectra must be especially broad due to the inhomogeneity of the matrix microstructure in the defect regions, begins to be retarded. It is probably for this reason that the transition of hydrogen bonds from the equilibrium of the frozen state occurs over a wide temperature range (100-200°). As the temperature falls off, the scale of molecular mobility decreases, and gradually degenerates to the γ-relaxation process, which is caused by the motion of the side radicals, whose structure is the same in PS and PMS. As a result, the equilibrium and hydrogen-bond system becomes completely frozen for both matrices at 220-240 (PS) and 180-210 K (PMS).

Complexes of PFP with ester groups of the active polymer matrix. Films of the MMA-St copolymer and its blends (up to 10%) with PS and PMS produced from solution were used as the active polymer matrix with ester groups being chemically linked to the polymer chain. In the ν_{OH} range the IR spectra of PFP introduced into the active matrix are identical with the spectra of the system considered above (Fig.1). The plots of the $\log(D^{AB}/D^{A})$ versus 1/T constructed on the basis of the spectroscopic measurements are given in Fig.3

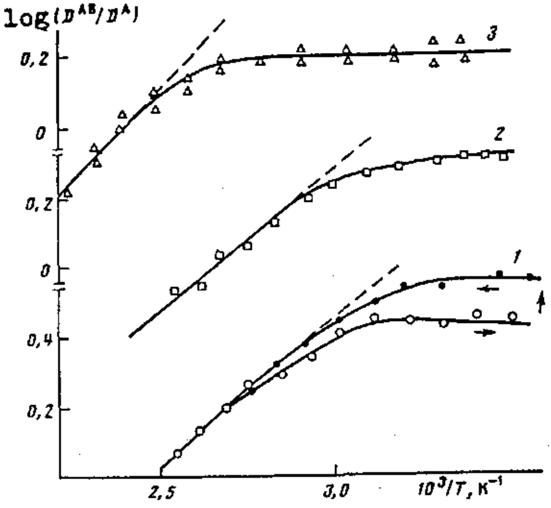

Fig. 3. Plot of the logarithm of the ratio of optical density of bound and free hydroxyl groups against 1/T for solutions of PFP in a methy methacrylate-styrene copolymer (1) and PFP and methyl methacrylate-styrene copolymer in PS (2) and PMS (3) matrices

Just as in the passive matrix, these plots consist of 3 portions. In the high-temperature range, the number of hydrogen bonds $C_6H_5OH...O=C$ increases in accordance with vant Hoff law as the temperature drops. At temperatures 40-60° below the T_g of each of the matrices of the hydrogen-bond system and begins to depart from the state equilibrium when the equilibrium is completely frozen upon further cooling of the samples. Transition to the non-equilibrium state for the MMA-St copolymer and the PS/MMA-St composition is observed at the same temperature. For the PMS/MMA-St composition this transition occurs at a temperature 50-60° higher than for the PS matrix. Hence, the formation and breaking of hydrogen bonds in the matrix is influenced by the structure and molecular dynamics of the polymeric chains of the matrix itself rather than by those of the incorporated macromolecules with active groups forming a hydrogen bond with PFP. Thus, the scale of molecular mobility both in the passive and the active matrix required for the establishment of the thermodynamic equilibrium state in the hydrogen-bond system corresponds to that beginning to the frozen in the temperature range of β-transition (~330 K for Ps and 380 K for PMS). However, whereas in the passive matrix the frozen state is realized over a rather wide temperature range, in the case of active matrices this range is much narrower (20-30°). This may be explained by the fact that the mobility of one of the partners in the formation of hydrogen bonds in the matrix (the ester group) is limited by the polymeric chain to which it is linked chemically, the distortions of the polymer microstructure of the degree of imperfection generated by a small PFP molecule being relatively small.

In the region of temperatures lying below that of β-transition in the matrix, the degree of nonequilibrium of the hydrogen-bond system depends on the previous history of the sample and rate of its cooling. As can be seen from Fig.3 (curve 3), the heating-cooling cycle with an unannealed film is accompanied by hysteresis phenomena. When the solvent is evaporated during film preparation a certain number of hydrogen bonds presumably are formed in the film, which is close to the equilibrium value at room temperature. After the sample is annealed above T_g the structure of the polymer matrix undergoes a change, the free volume decreases and upon subsequent cooling at a finite rate the system has no time to follow the change in temperature and becomes nonequilibrium at a higher temperature than in the case of the unannealed sample. However, as the time progresses, the number of hydrogen bonds increases, tending to the equilibrium value. The kinetic measurements performed on samples subjected to hardening in liquid nitrogen and rapidly heated up to 25°C show that the value of the log (D^{AB}/D^{A}) increases with time by an exponential law, this indicating the relaxational character of the process of formation of hydrogen bonds in the polymer matrix.

REFERENCES

1. A. Barkatt and C.A. Angell, J. Chem. Phys., 70,2, 901 (1979).
2. Y. Kihira, J.Sci. Hiroshima Univ., Ser. A40, 2, 293 (1976).
3. S.N. Zurkov and B.Ya. Levin, Dok. Akad. Nauk SSSR, 72, 2, 269 (1950).
4. G.S. Denisov, A.I. Kul'bida and V.M. Shraiber in: Molecular Spectroscopy, Izd. LGU, Leningrad, 6, (1983).
5. A.G. Zak et al, Izv.Vuz.Khim. i Khim. Tekh., 18, 6, 951 (1975).
6. G.V. Gusakova et al, Khim.Fiz., 2, 12, 1690 (1983).
7. A.L. Smolyanskii in: Optics and Spectroscopy. II. Molecular Spectroscopy, Nauka, Moscow-Leningrad, 1963.
8. V.A. Bershtein and V.M. Yegorov, Vysokomolek. Soedin. A27, 11, 2440 (1985).