

FTIR spectroscopy of conformational probes introduced into binary blends of polymers

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Abstract. In this paper we considered the behaviour of the conformational probes introduced in polymer blends. The temperatures of the secondary relaxation transitions of the binary blends of polyvinyl butyral and polyethylene glycol were determined by FTIR spectra. The assignment of the secondary relaxation transitions to the types of local molecular mobility in the blend of polymers was carried out.

1. Introduction

Many physical and chemical properties of polymeric materials are due to local molecular dynamics of polymeric chains. One important characteristic of molecular mobility in polymers is the secondary relaxation transitions that appear below the glass transition temperature. They correspond to the “unfreezing” of the internal rotation of side groups and other fragments (relaxators) of the polymer chain when temperature increases. The method of FTIR spectroscopy of conformational probes allows determination of the temperature of relaxation transitions and assigning them to specific relaxators, the swing isomer mobility of which facilitates the diffusion of separated gases in polymer membranes, protective layers and coatings [1].

The blending of polymers is one of the methods of modification of properties of polymeric materials. This method allows one to create unique micro- and nanoscale structure that are not available in the case of the use of one-component systems. The directional change in composition of the polymer blend is an effective regulation method of the porous structure, morphology, crystallinity, and other characteristics of the polymeric material [2].

Presently, various blends of individual polymers are widely studied because new membrane materials possessing different functions can be made of them. For example, the use of binary mixes of polyvinyl butyral (PVB) with other polymers is of interest. It allows one to receive materials with new operational properties [3]. PVB in combination with polyvinylidene fluoride for creation of new ultrafiltration and microfiltration membranes was studied in [4]. It is known that individual PVB, which is thermoplastic, is used for the manufacturing of new and inexpensive porous membranes having thermal and chemical resistance. Polyvinylidene fluoride is a thermoplastic fluorinated polymer and it is characterized by high chemical stability in wide temperature ranges.

The purpose of this work is the IR spectroscopic investigation of the local molecular dynamics of the binary blends of polymers PVB and polyethylene glycol (PEG). We study the polymer blends with different percentage ratio of its polymers. We use the conformational probes to determine the temperature of secondary relaxation transitions of the polymer blends.



In liquid and solutions, the probe molecules are in two conformations (*trans* and *gauche*), between which a dynamic equilibrium may be established. Two analytical bands are identified in the IR spectrum of the probe, relating to the *trans* and *gauche* conformations. For their integral optical density D , the Beer–Lambert–Bouguer law is implemented:

$$D_{trans} = \alpha_{trans} l c_{trans}, \quad D_{gauche} = \alpha_{gauche} l c_{gauche},$$

where α_{trans} and α_{gauche} are the integrated absorption coefficients of the respective bands, l is the thickness of the absorbing layer, and c_{trans} and c_{gauche} are the concentrations of *trans* and *gauche* conformations. The concentration ratio is determined by equilibrium constant K , which depends on the temperature:

$$K = c_{trans}/c_{gauche} = \exp(-\Delta G_0/RT),$$

where ΔG_0 is the difference in free energy of conformations, which can be represented as the difference between the enthalpy and entropy terms: ΔH_0 and ΔS_0 is the difference of the enthalpy and entropy of conformations, respectively. For the ratio of the optical densities of analytical absorption bands of *trans* and *gauche* conformations, we have

$$\ln(D_{trans}/D_{gauche}) = \ln(\alpha_{trans}/\alpha_{gauche}) - \Delta H_0/RT + \Delta S_0/R + \text{const.}$$

One can determine temperature T_f , at which conformational transitions of the probe in the polymer are frozen. In this case, the considered dependence in the temperature range of $T < T_g$ will consist of two branches intersecting at the temperature of T_f .

2. Experimental

PVB (Butvar B-98) and PEG (molecular weight 10,000) were manufactured by Sigma-Aldrich. PEG is an amorphous-crystalline polymer. It means a presence of both amorphous and crystalline parts. Structural formula of monomer units of these polymers are shown in figure 1.

The mixes of PVB/PEG with polymer compositions 80:20 and 60:40 were obtained by the method of physical mixing. They were prepared by dissolving the PVB and PEG in chloroform. The obtained solution was spread on KBr plates. The films were dried at room temperature for several days to evaporate the solvent completely. The absence of solvent in the samples was fixed by IR spectra.

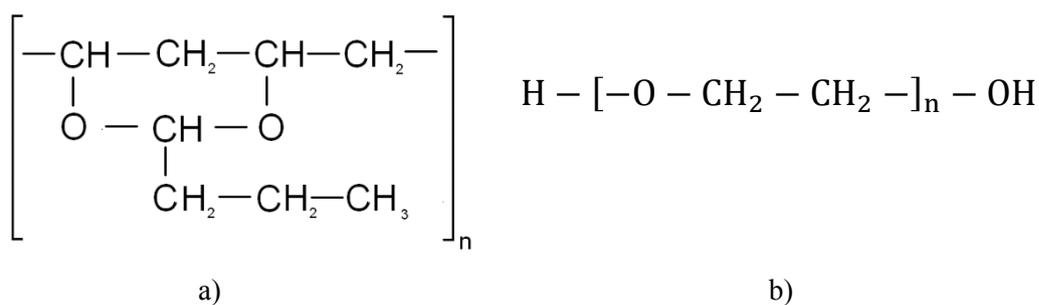


Figure 1. Structural formula of monomer units of polyvinyl butyral (a) and polyethylene glycol (b).

Following conformationally-inhomogeneous probes were used: 1,2-diphenylethane (DPE); 1,2-dichloroethane (DCE); 1,1,2,2-tetrabromoethane (TBE), 1,1,2,2-tetrachloroethane (TCE), 1,2-diparabromophenylethane (DPBPE). The probes were chosen so that the absorption bands of the probes fall in the transparent area of the components of the binary polymer blend. However, if there was an overlapping of analytical absorption bands of probe and polymers then the subtraction of the spectrum of a blend from spectrum of system probe + polymer mixture was carried out.

Analytical absorption bands were the following conformation-sensitive absorption bands of probes at 616, 638 and 585 cm^{-1} for TBE; at 655 and 710 cm^{-1} for DCE, at 580 and 700 cm^{-1} for DPE; at 545

and 756 cm^{-1} for TCE; 538 and 518 cm^{-1} for DPBPE. TCE, DCE and TBE were introduced into polymer mixture from gaseous phase. DFE and DPBPE were introduced into the blend from the solution in chloroform. The probe concentrations were 1-3 wt. %. The concentration of the probe and the thickness of the absorbing layer were calculated by IR spectra. We used the cryostat Specac cooled by liquid nitrogen. Fourier-transform infrared spectra were recorded with a Perkin Elmer FTIR spectrometer Frontier.

3. Results and discussion

FTIR spectra of the conformational probes DCE, TBE, TCE, DPE and DPBPE in the polymer blends of PVB and PEG with polymer compositions 80:20 and 60:40 at different temperatures from 300 to 100 K were obtained. Figure 2 shows FTIR spectra of the system PVB/PEG (80:20) and DCE at three different temperatures. These spectra demonstrate a change of intensities of the conformation-sensitive (*gauche* and *trans*) absorption bands of the probe in the polymer when temperature decreases. The dependencies of logarithm of the ratio of the intensities (optical densities) of the conformationally-sensitive absorption bands upon the inverse temperatures in polymer blends showed the presence of freezing of conformational equilibria of probe's molecules in the studied temperature range. These dependencies for all probes in the polymer blends consist of two branches which cross at the freezing temperature T_f of conformational equilibrium of the probe in the polymer blend (figure 3). Besides, FTIR spectra of the probes DCE, TBE and DPE were obtained for pure PEG in the same temperature range (figure 4 and 5). Freezing of conformational mobility of the probe molecule is related to the average size of the cavity in the polymer, which is close to the size of the rotational fragment of the probe molecule V_p^\ddagger .

The freezing temperature T_f for the polymer blends were obtained as well as T_f for individual PEG. For individual PVB the temperatures T_f were obtained in [5] and compared with the relaxation transitions. It is shown that the temperatures T_f characterize the relaxation transitions associated with the internal rotation of C_2H_5 and C_3H_7 side groups of the polymer chain.

As to assignment of the freezing temperatures T_f to the types of mobility of the polymer chain for PEG, we consider the macromolecule of polyvinylchloride (PVC). PEG macromolecule has the structure similar to the structure of macromolecule of PVC which is also an amorphous-crystalline polymer. Besides, the monomer unit of PVC does not contain side groups. It is shown in [6] that the conformational mobility of the different probes in PVC is stopped at different temperatures, indicating the presence of several secondary relaxation transitions in PVC. When considering the local dynamics of PVC macromolecules, it is possible to distinguish three types of relaxations in the studied range of temperatures: one type is connected with torsional vibrations of CHCl fragment and two types are connected with motions of one and two monomeric units by the "crankshaft mechanism" [6]. It is assumed that there is also the local mobility of "crankshaft" in PEG. Such mechanism is also likely because the axis of rotation in PEG macromolecule is the C-O bond which has not the substituents inhibiting rotation.

Generally, the mechanism considered above for local mobility is only possible in an amorphous polymer or in amorphous regions of partially crystalline polymers. That is due to the fact that the motion of "crankshaft" type only occurs with respect to two collinear bonds. This condition is not satisfied in the crystalline regions where the sequences of methylene groups form mainly the planar *trans* conformation [7].

The freezing temperatures for the polymer blends were slightly higher than for individual PVB, namely, for DCE $T_f = 210$ and 195 K in PVB /PEG (60:40) and (80:20), respectively, as compared to 180 K in PVB; for TCE $T_f = 230$ and 235 K in these blends as compared to PVB at 225 K . For TBE the temperatures T_f are close to the mean magnitude of 240 K in both blends as compared to PVB at 235 K . For DPE $T_f = 260\text{ K}$ in the blend (60:40) as compared to 240 K in PVB and for DPBPE $T_f = 250\text{ K}$ in both blends as compared to 240 K in PVB.

As to the assignment of the temperatures T_f associated with relaxation transitions in the polymer blends, it is necessary to estimate the van der Waals' volume of mobile fragments (relaxators) of

polymer chain of PVB and PEG by the additive scheme [8]. The evaluation gives the following volumes of the mobile fragments (relaxators) and the effective sizes of free volume elements. The relaxators C_2H_5 and C_3H_7 in PVB have volumes 27 and 44 \AA^3 , respectively. The volumes of fragments of polymeric chain of two "crankshaft" types, containing CH_2-CH_2-O and $CH_2-CH_2-O-CH_2$ groups, are equal to 44 and 64 \AA^3 for PEG, respectively. Furthermore, it can be assumed that at the temperature of 190 K the mobility of $H-O-CH_2$ group with the volume equaled to 26 \AA^3 .

Thus, the IR spectroscopic method of conformational probes allows us to study the local molecular mobility in the binary polymer blends which may be used as the membranes for microfiltration and ultrafiltration.

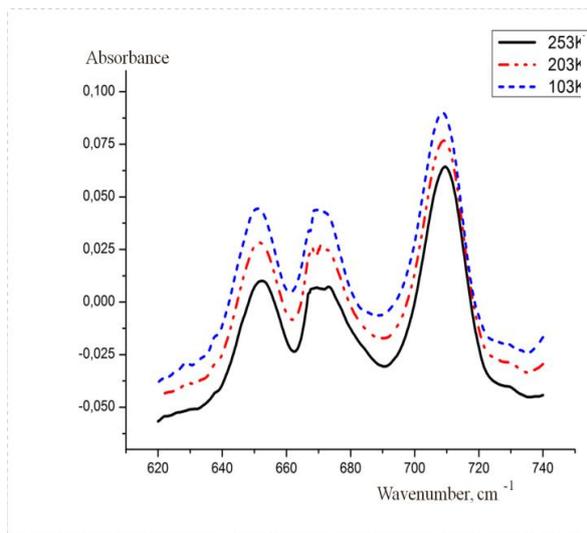


Figure 2. Fragments of FTIR spectra of DCE in PVB/PEG (80:20) at three different temperatures.

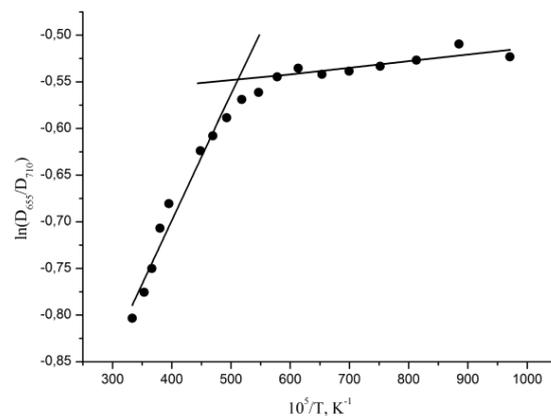


Figure 3. Dependence $\ln(D_g/D_t)$ on $1/T$ for DCE in PVB/PEG (80:20).

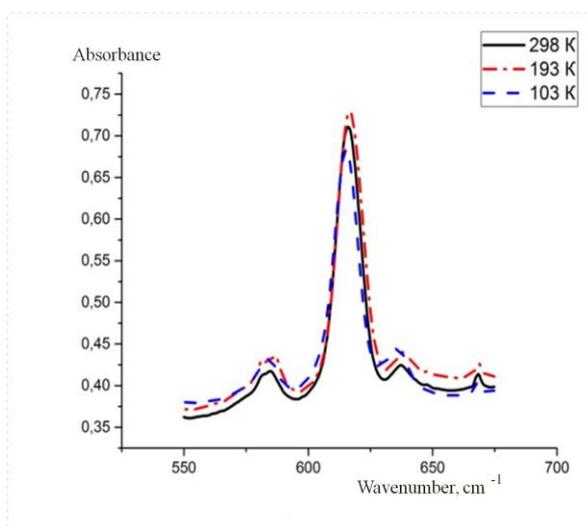


Figure 4. Fragments of FTIR spectra of TBE in PEG at three different temperatures.

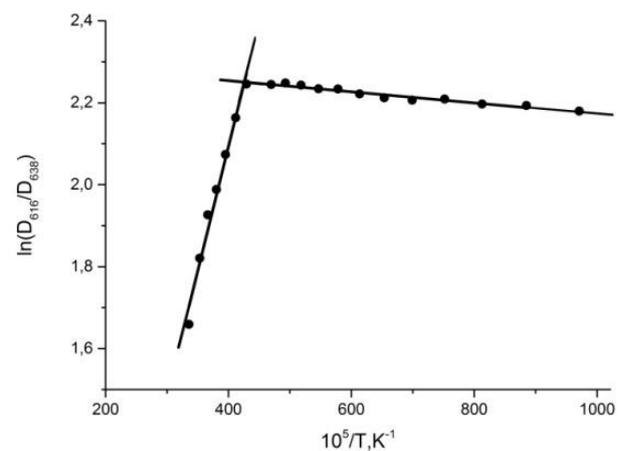


Figure 5. Dependence $\ln(D_g/D_t)$ on $1/T$ for TBE in PEG.

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