

Binary Polymer Systems Based on Polyvinylbutyral: FTIR Spectra, Conformational Dynamics, and Free Volume

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Abstract—Local molecular dynamics of polymer systems based on polyvinylbutyral is studied via the IR Fourier spectroscopy of conformation-inhomogeneous probes. The compositions of the studied binary mixtures of polyvinylbutyral with polymethylmethacrylate are 80 : 20, 60 : 40, 40 : 60, and 20 : 80. The temperatures of the secondary relaxation transitions and the difference between the enthalpies of conformation of the probe molecules in these systems are obtained. The effective sizes of mobile free-volume elements, the diffusion of which results in the transport of small molecules upon membrane gas separation, are estimated.

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INTRODUCTION

Binary polymer systems are widely used in membrane separation processes [1–3]. The principle of separation membrane operation is based on the difference between the permeability of a membrane's working layer with respect to the components of the initial mixture. The driving force of the process can be the difference in concentrations, pressures, temperatures, or electrical potentials on opposite sides of the membrane. It should be noted that a membrane is not an ideal selectively permeable barrier [4].

Membranes are divided onto porous and nonporous, according to the structure of their material. The porous type contains macropores, and it is the pore size or pore size distribution that determines which particles or molecules are retained by the membrane and which pass through it. As for their separation characteristics, they depend only slightly on the nature of the membrane material. Nonporous (dense) membranes, which are used mainly for gas separation, have no fixed pores, and the operating characteristics of these membranes are determined by their material. The polymer structure determines the diffusion of the components to be separated. Diffusion is in turn associated with the local mobility of the polymer chain, i.e., with the rotation or turns around bonds. Studying the structure and dynamics of polymers is thus a key element in developing new materials with high coefficients of both permeability and selectivity.

Porous membranes separate gases due to the presence of even smaller (in comparison to pores) free-volume elements that, according to [5], consist of mobile and stationary holes. Mobile holes form due to the thermal mobility of the polymer chain and its fragments, while fixed holes are due to the nonequilibrium

structure of the glass-like polymer matrix. It should be noted that we are not talking here about the deep separation of gas mixtures, since the kinetic diameters and average free path of gas molecules are small even in comparison to the pores of minimal size.

Polyvinylbutyral (PVB) is a porous polymer categorized as thermoplastic and is used to manufacture inexpensive porous membranes that have thermal and chemical resistance. Binary mixtures of PVB and other polymers, particularly polymethylmethacrylate (PMMA), are of interest in obtaining materials with new physical properties [6–8].

The aim of this work was to study the local conformational dynamics and free volume distribution in binary polymer systems based on mixtures of PVB and PMMA at different ratios of the components, and to compare the results to the distribution of free-volume in individual components.

CONFORMATIONAL PROBES

The flexibility of polymer chains is closely related to the effect of internal rotation in macromolecules, which occurs around simple chemical bonds [9]. Such mobility of individual kinetic units of the macromolecule is known as local molecular mobility. Each type of local mobility is frozen at a certain temperature. This temperature, which differs for each polymer, is determined by the chemical structure and structural features of the material [10].

IR spectroscopy with conformation inhomogeneous probes [5] extends the possibilities of studying the local dynamics of polymers, their relaxation transitions, and the distribution of the free volume inside them. Briefly, molecules of the probe that are intro-