

# Small conformationally mobile molecules as probes for molecular mobility in glassy polymers

A. A. Stolov\*, D. I. Kamalova, A. B. Remizov and O. E. Zgzadzi

Department of Chemistry, Kazan State University, Lenin Street 18, Kazan, 420008, Russia  
(Received 26 October 1992; revised 18 November 1993)

A new method for studying molecular mobility in glassy polymers—the method of conformationally inhomogeneous probes—is described. A small quantity of a low-molecular-weight compound (probe) having unidentical conformations with different vibrational spectra is introduced into a polymer. The thermodynamic and activation parameters responsible for the concentrations of the conformers and the rates of conformational transitions are connected with both the intramolecular interactions and the properties of the medium (e.g. polymer). Information about the kinetics and equilibria of the conformers could be obtained by investigating the vibrational spectra. This information may be the key to understanding the molecular mobility and free-volume distribution in polymers. The following compounds were used as probes: 1,2-bromofluoroethane, methyl dichlorophosphate and *trans*-1,2-dichlorocyclohexane. The polymers polystyrene, poly(vinyl chloride), poly(methyl methacrylate), poly(vinyl acetate), poly(vinylbutyral), polypropylene and polybutadiene were investigated. The temperature dependences of the absorption-band intensities of the probes were studied. Freezing of the conformational transitions in the probe molecules was found at temperatures  $T_f$  characterizing specific polymer–probe systems. The  $T_f$  are close to the temperatures of the relaxation transitions in the pure polymers. The possibilities of the method are discussed.

(Keywords: glassy polymers; molecular mobility; conformationally mobile probes)

## INTRODUCTION

Molecular mobility and the distribution of free volume in glassy polymers have been intensively studied by different physical methods. The methods of dielectric, mechanical and acoustic relaxation<sup>1–12</sup> and differential scanning calorimetry<sup>13,14</sup> are the most developed. The spectroscopic methods (n.m.r.<sup>1,15,16</sup>, excimer fluorescence spectroscopy<sup>17</sup>, far-i.r. spectroscopy<sup>18,19</sup>) are also widely used. Methods based on the use of molecular probes are numerous. The mobilities of spin<sup>20</sup>, electrochromic<sup>21,22</sup>, fluorescence<sup>23,24</sup>, excimer-forming<sup>25,26</sup> and photochromic<sup>27,28</sup> probes, the kinetics of proton transfer in polymers<sup>29,30</sup> and the kinetics of ring closure of merocyanine<sup>31</sup> have been studied. The great number of approaches indicates, on the one hand, that interest in studying molecular mobility in polymers grows and, on the other hand, that a universal approach to this problem is absent. The various physical methods are aimed at investigating different aspects of molecular mobility, and their data are complementary.

Earlier<sup>32</sup> we proposed a new approach to study molecular mobility in glassy polymers, which is based on the investigation of the conformational mobility of small molecules introduced into polymers. The present paper is devoted to describing the approach and discussing the results obtained up to now.

## METHOD OF INVESTIGATION

The basis of the approach is as follows. A small quantity of low-molecular-weight compound (probe) having at least two unidentical stable conformations A and B in dynamic equilibrium:



is introduced into the polymer. Here  $K$  is a conformation equilibrium constant. Classic examples of the compounds in question are 1,2-disubstituted ethanes having two stable conformers, *trans* and *gauche*. The value of the equilibrium constant is determined by the relation:

$$K = \exp(-\Delta H_0/RT + \Delta S_0/R) \quad (2)$$

where  $\Delta H_0$  and  $\Delta S_0$  are the enthalpy and entropy differences of the conformers. The rate of the conformational transitions is determined by activation free enthalpy  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ , where  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the enthalpy and entropy of activation. The values  $\Delta H_0$ ,  $\Delta S_0$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are connected with both the intramolecular interactions and the properties of the medium (e.g. polymer). Hence, information about the structure and molecular mobility of the polymers may be obtained by investigating the thermodynamic and kinetic parameters of the probe conformations.

The shift of the conformational equilibrium and the rate of the conformational transitions may be registered by infra-red spectra. According to the Lambert–Burger–

\* To whom correspondence should be addressed