

FTIR spectroscopy of conformational probes introduced into fullerene-containing branched poly (methyl methacrylate)

L R Abdrazakova and D I Kamalova

Kazan Federal University, Kazan 420008, Russian Federation

E-mail: dina.kamalova@kpfu.ru

Abstract. In this paper we consider the effect of fullerene on the local molecular dynamics of the branched poly (methacrylates). The temperatures of the secondary relaxation transitions were determined by FTIR spectra. It was shown that there is the secondary relaxation transition at 190 K in copolymer containing C_{60} , while there are the relaxation transitions at 230 and 190 K in same copolymer without fullerene.

1. Introduction

Branched polymers have unique properties: high solubility in non-aqueous media, low viscosity as compared with linear polymers, high sorption capacity and ability to transport low-molecular substances. A linear (nonbranched) poly (methyl methacrylate) (PMMA) is widely used in mechanical engineering, instrumentation, medical industry, household products, and branched copolymers of methyl methacrylate are used as nanocontainers of functional additives in the synthesis of the polymers with new properties. The study of the structure and internal dynamics of branched polymers is relevant and contributes to the development of modern ideas about the fundamental physical properties of macromolecules.

Branched polymers have a large number of lateral groups and compact globular structure in solutions as compared with the linear ones. Due to the unusual topology, branched polymers have good compatibility with different polymers, excess free volume and ability to absorb substances inside macromolecules according to the "host-guest" type.

The addition of fullerene C_{60} as a nanomodifier to branched polymers by covalent and noncovalent bonding leads to a new complex of useful properties and, thus, opens further prospects of its application as new materials with electrical, magnetic and optical properties [1]. Along with diamond, graphite and carbon nanotubes fullerene is allotropic form of carbon. The main advantage of fullerene are its high electron-acceptor properties and the ability to synthesize various chemical derivatives. It is mostly used in pharmacology. A series of derivatives of fullerene C_{60} with pronounced membranotropic, antioxidant, antiviral and immunomodulatory properties has been developed. This has opened the way to the use of fullerene for effective therapies and vaccines [2, 3]. It is known that fullerene is an effective nanomodifier; its small additive significantly improves the operational properties of different polymers [4].

The purpose of this work is IR spectroscopic study of the local molecular dynamics in glassy branched poly (methacrylate) (BPMMA) and its fullerene-containing analogue (FBPMMA) by the method of conformational probes [5]. This method is based on investigating conformational



behavior of a low-molecular-weight compound introduced as a probe into an amorphous glassy polymer. The value of the equilibrium constant K is determined by the expression:

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

where ΔH_0 and ΔS_0 are the enthalpy and entropy differences of the conformers. The values ΔH_0 and ΔS_0 depend on intramolecular interactions in the probe molecule and dynamic properties of the medium (e.g. polymer). Hence, the information about structure and local mobility of polymers can be obtained by investigating thermodynamic and kinetic parameters of the probe molecule conformations.

A decrease of the temperature causes a redistribution of conformer's concentrations, i.e. a shift of conformational equilibria. Consequently, the intensities of conformer IR-bands are redistributed. According to the Beer's law, one may write the following expression for the integrated intensities I_t and I_g of the absorption bands of the *trans* and *gauche* conformers:

$$\ln(I_t / I_g) = \ln(\alpha_t / \alpha_g) - \Delta H_0 / RT + \Delta S_0 / R = \ln K + \ln(\alpha_t / \alpha_g),$$

where α_t and α_g are the integral absorption coefficients of the utilized bands. If there are conformational transitions in the system and $\Delta H_0 \neq 0$ then the experimental value $\ln(I_t/I_g)$ must depend on the temperature. The ΔH_0 value characterizes a slope of this dependence. If a low-molecular-weight compound is added to a polymer as a probe, then the values ΔH_0 , ΔS_0 will also depend on macromolecular structure and local molecular mobility of polymer. If at a certain temperature, T_f , the conformational transitions freeze, it is definitely due to a process taking part in the polymer. Comparing the structure of the rotational fragments of probe and the polymer, one may get an idea about the type of secondary relaxation transitions [5].

2. Experimental

Branched copolymer of methyl methacrylate (MMA) with allyl methacrylate (AMA), which was obtained under conditions of the transmission of chain (chain transfer agent - 1 decantiol, DT) was investigated. The composition of the initial monomeric mixture of MMA / AMA / DT is equal to 100: 5: 5 mol %. Methyl methacrylate copolymer of the same composition but containing C₆₀ was investigated too. The glass transition temperatures are 347 and 340 K for BPMMA and FPMMA, respectively.

We used the conformationally-inhomogeneous probes: 1,2-diphenylethane (DPE); 1,2-dichloroethane (DCE); 1,1,2,2-tetrabromoethane (TBE) which exist in two conformations in liquids and solutions. The volumes V_p^\ddagger of small rotational fragments of the probe molecules estimated by an additive scheme are the following: 24 (DCE), 57 (TBE) and 86 (DPE) Å³. 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. These bands are located in the transparent region of the polymers.

Films were prepared by dissolving a polymer in chloroform. The solutions were 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. 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

The FTIR spectra of the probe+polymer system for three different temperatures are represented in figure 1. 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. Similar spectra were obtained for the other systems: probe+BPMMA and probe+FPMMA. The dependencies of logarithm of the ratio of the intensities of the conformationally-sensitive absorption bands upon the inverse temperature were plotted (figure 2). Such dependencies for all probes in branched copolymers consist

of two branches which cross at the freezing temperature of conformational equilibrium of the probe in the polymer (T_f). The values of obtained temperatures for BPMMA are 195 ± 10 K (DCE), 230 ± 10 K (TBE) and 225 ± 20 K (DPE). The values of temperatures T_f for FPMMA are 190 ± 15 K (DCE), 190 ± 10 K (TBE) and 205 ± 10 K (DPE). The freezing temperature of conformational equilibrium of the probe in the polymer reflects the secondary relaxation transition in this polymer.

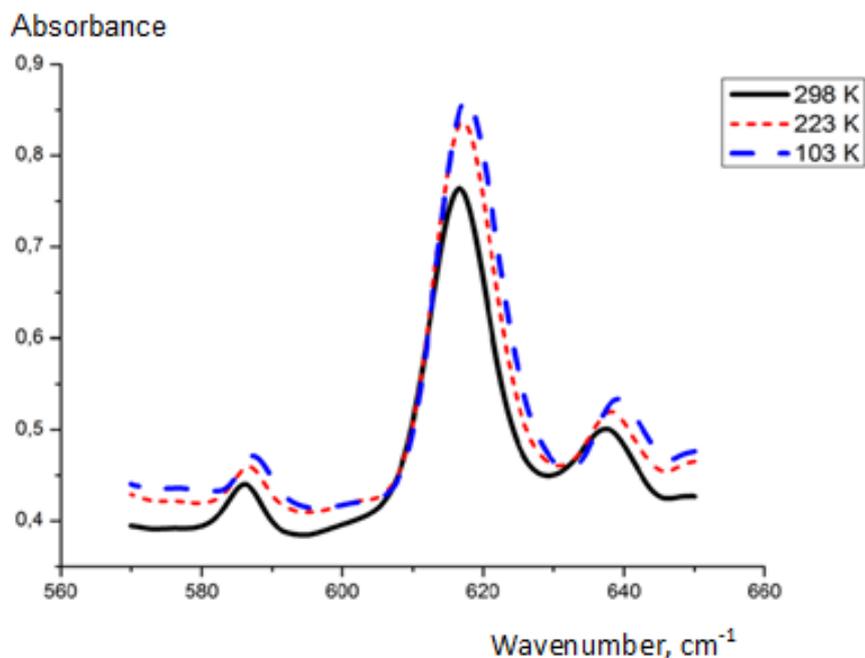


Figure 1. Fragments of FTIR spectra of TBE in BPMMA at different temperatures.

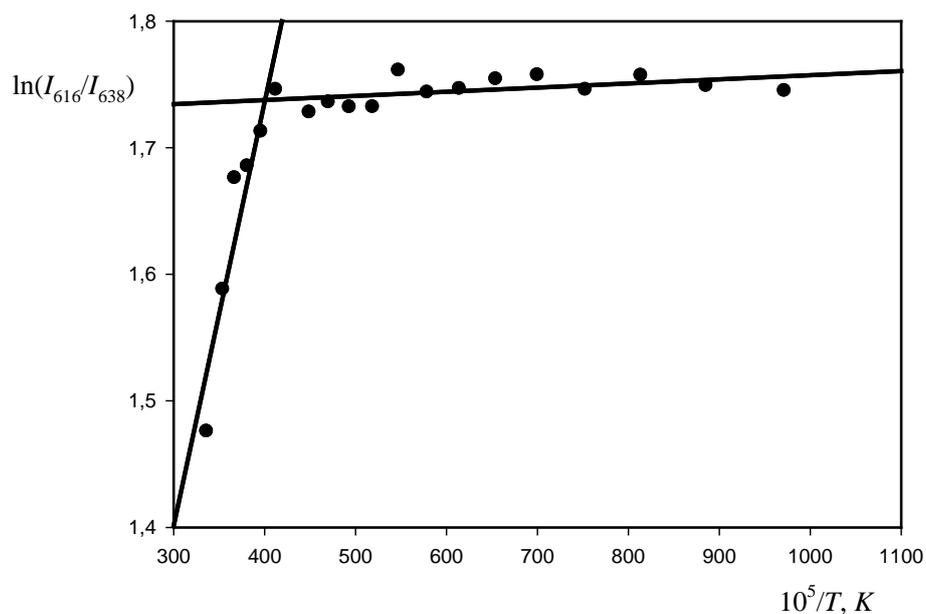


Figure 2. Dependence $\ln(I_g/I_i)$ on $10^5/T$ for TBE in BPMMA.

Freezing of conformational mobility of the probe 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). Comparing of the freezing temperatures of conformational mobility of the probes in branched and linear polymers indicates that in branched copolymers BPMMA and FPMMA there is the same relaxation transition ($T_f = 190$ K) as linear PMMA. Besides, the relaxation transition ($T_f = 230 \pm 10$ K) occurs in BPMMA approximately as in linear PMMA (240 ± 10 K). When we used all three conformational probes having different activation volumes (from 24 to 86 Å³) we have obtained only one relaxation transition in the copolymer with fullerene. Fullerene molecules consist of 60 carbon atoms and have the compact spheroidal shape. Each fullerene molecule occupies very large volume (approximately 190 Å³) as compared with the volume of activation of conformational probes. Covalently bonded fullerene exerts loosening influence on branched copolymer. This influence is such that the conformational mobility of the largest fragment of the used probe is frozen at the lowest temperature.

The authors thank S.V. Kurmaz (Institute of Problems of Chemical Physics of the Russian Academy of Sciences) for the provision of polymer samples.

References

- [1] Kurmaz L V and Ozhiganov V V 2011 *High-molecular connections* **53** 394-409
- [2] Anufrieva E V and Krakowiak M G 2002 *Solid State Physics* **44** 443-444
- [3] Salikhov T H , Tabarov S H , Rashid D A *et al* 2009 *Letters to the Journal of Technical Physics* **35** 75-78
- [4] Zgonnik V N and Vinogradov L V 2002 *Solid State Physics* **44** 592-593
- [5] Kamalova D I *et al* 2008 *Konformatsionnie zondi v izuchenii lokalnoi podvizhnosti polimerov* (Moscow: Fizmatkniga)