MOLECULAR DYNAMICS AND HETEROGENEITY OF THE STYRENE-ACRYLONITRILE COPOLYMERS AS VIEWED BY ELECTRON SPIN RESONANCE[†]

Mladen Andreis[1], Zorica Veksli[1], Marko Rogošić[2] and Helena Jasna Mencer[2]

[1]*Ruđer Bošković Institute, Bijenička c. 54, HR-10000 Zagreb, Croatia*

[2]*Faculty of Chemical Engineering and Technology, University o Zagreb, Marulićev Trg 19, HR-10000 Zagreb, Croatia*

Abstract

Molecular mobility and heterogeneity of statistical and alternating copolymers of styrene and acrylonitrile have been studied in the wide temperature range by the ESR spin probe method using two nitroxyl radicals, Tempo and Tempone. The temperature at which the maxima separation becomes 5 mT decreases with increasing styrene content. At higher temperatures above the glass transition temperature the copolymers with the smaller amount of styrene reflect motional heterogeneity. The motional difference between the statistical and alternating copolymers of a similar composition are reconciled on the basis of the sequence structure of copolymer chains. The packing of segments and the formation o motionally different domains can be explored by the adequately chosen probe even i the homopolymers have very similar glass transition temperature but differ in the polar and packing features.

Introduction

Copolymers of styrene and acrylonitrile (SAN) have been widely studied and used due to their unique properties such as dimensional stability, long-term toughness, high craze resistance and chemical resistance. These properties depend on the monomer pai composition. When SAN composition vary significantly, the copolymers become

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[†] Dedicated to the memory of Professor Dr. Anton Šebenik

immiscible [1]. Therefore, it is important to maintain compositional and local homogeneity. However, packing details and segmental mobility of copolymer chains differing in the monomer pair composition have not been investigated thoroughly. One of the methods which can offer an insight into the heterogeneity of copolymers and polymer blends is electron spin resonance (ESR) using nitroxyl spin probes.

The spin probe method applied to synthetic polymers has been shown to be a useful tool in the study of local morphology and segmental dynamics under different conditions [2]. The aim of this paper is to study heterogeneity and segmental motion in copolymers of the same monomer pairs but of different composition. Two spin probes are applied to investigate how the type of a probe can monitor free volume generation with temperature. Special attention is focused on the segmental dynamics and packing depending on the loca copolymer sequence structure in alternating and statistical copolymers having similar molar ratio of monomer pairs.

Experimental section

Materials. Homopolymers of polystyrene (PS) and polyacrylonitrile (PAN) and statistical copolymers of styrene- acrylonitrile containing 54 (SAN-54S), 90 (SAN-90S) and 10 (SAN-10S) mole % of styrene, respectively, were prepared by radical solution polymerization. The reactions were carried out in a batch isothermal reactor (250 c^3 of total volume) at 333 K. Monomer components of styrene (INA-OKI, Zagreb, Croatia) and acrylonitrile (OHIS, Skopje, Macedonia) distilled prior to (co)polymerisation were mixed using N,N-dimethylformamide (DMF, Merck) as a solvent. The initiator azobisisobutyronitrile (AIBN, AKZO Chemie, The Netherlands) was added in the concentration of 0.01 d^3. The reaction mixture was constantly nitrogen-stirred and the polymer was precipitated in cold methanol and purified by dissolution in DMF and reprecipitated in methanol. The alternating copolymer styrene- acrylonitrile containing 49 mole % of styrene (SAN-49A) was prepared in the bulk using $ZnCl_2$ as a complexing agen [3]. The molecular weights were measured by GPC and/or diluted solution viscometry, whereas the copolymer composition was determined by the "micro-Dumas" method. The

range of molecular weights is between 8×10^4 and 3×10^5. The statistical and alternating SAN copolymers with approximately 50 mole % of styrene contain about 36% and 12% of heterotactic copolymer units (SSA and AAS), respectively, as calculated from th ^{13}C NMR spectra [4].

ESR measurements. The polymers were doped with 4-oxo-2,2,6,6-tetramethyl-1-piperidinyl-oxy (Tempone) and 2,2,6,6-tetramethyl-1-piperidinyl-oxy (Tempo) in tetrahydrofurane (THF) and N,N-dimethylformamide (DMF) solution in the case o polyacrylonitrile and acrylonitrile rich copolymers. The concentration of spin probes did no exceed 0.02 mass%. The ESR spectra were recorded on a Varian E-109 X-band spectrometer operating at 100 kHz modulation. A variable temperature unit controlled the temperature.

Results and discussion

The temperature dependent ESR spectra o nitroxyl radical incorporated into the polymer matrix offer an ability to correlate nitroxyl motion with the microscopic
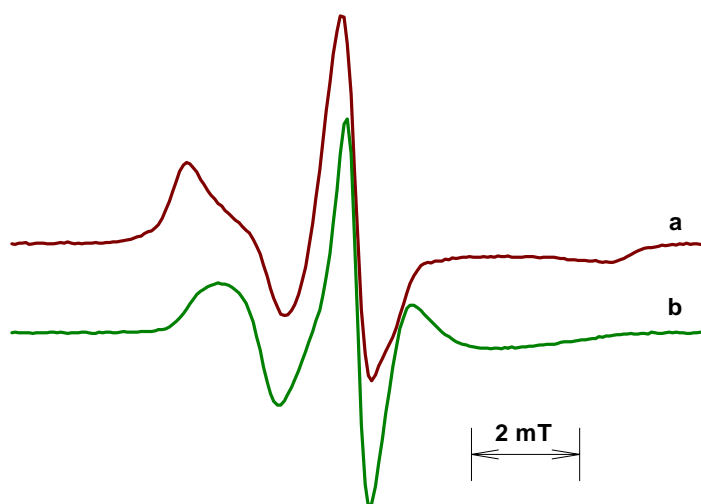

Figure 1. ESR spectra of PS doped with Tempone at (a) 253 and (b) 353 K.

polymer environment. Representative ESR spectra of doped polystyrene (a) below and (b)

above the glass transition temperature, T_g, are shown in Figure 1. In order to compare mobility of spin probes in homopolymers of polystyrene, polyacrylonitrile and their copolymers in a semiquantitative way, the maxima separation, $2A_{zz}$, of the ESR spectra is plotted versus temperature (Figure 2 and Figure 3). The maxima separation reflects the mobility of spin probes and decreases with an increase of the mobility. Temperature at which $2A_{zz}$ of a typica sigmoidal curve becomes 5 mT, defined as T_{5mT}, is empirically correlated with the glass transition temperature [5,6]. In the case when the spectra are superposition of a slow and fast component, the dashed lines represent estimated values of the two maxima separation. T_g reflects the macroscopic character of the segmental motion of polymer chains, while T_{5mT} gives information on the microenvironment around the probe molecule through its mobility. The motional
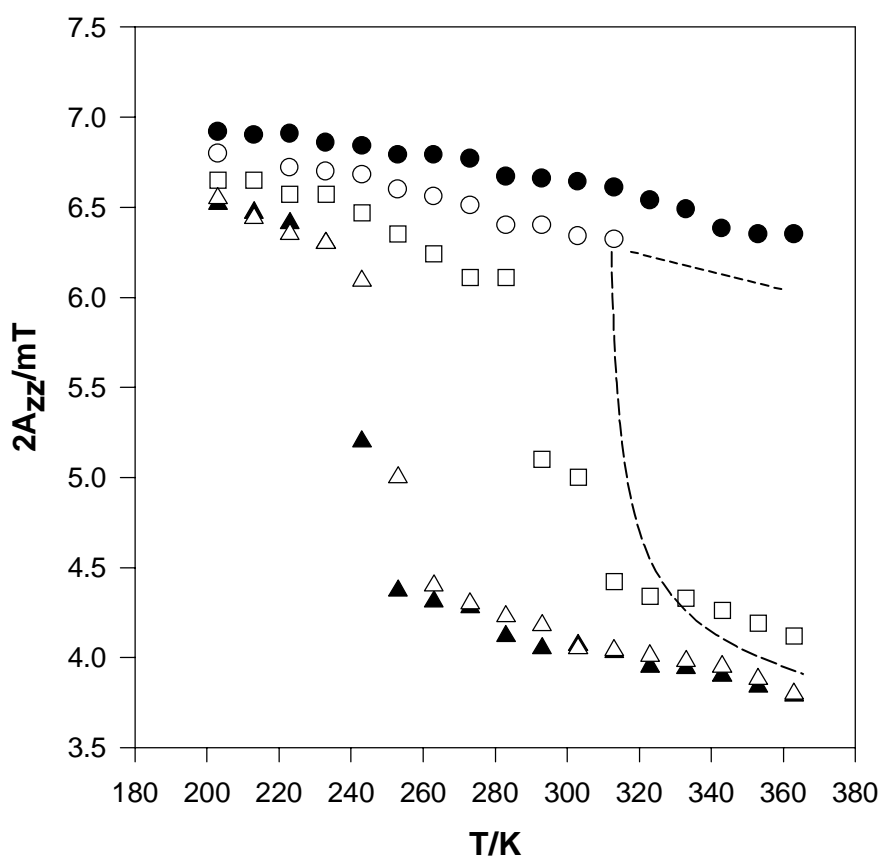

Figure 2. Temperature dependence of the maxima separation ($2A_{zz}$) for samples: PAN ($\square$), SAN-10S ($\circ$), SAN-54S ($\square$), SAN-90S ($\triangle^a$) and PS ($\blacktriangle$) probed with Tempo.

Figure 3. Temperature dependence of the maxima separation ($2A_{zz}$) for samples: PAN (□), SAN-10S (○), SAN-54S (□), SAN-90S (^{a}) and PS (▲) probed with Tempone.
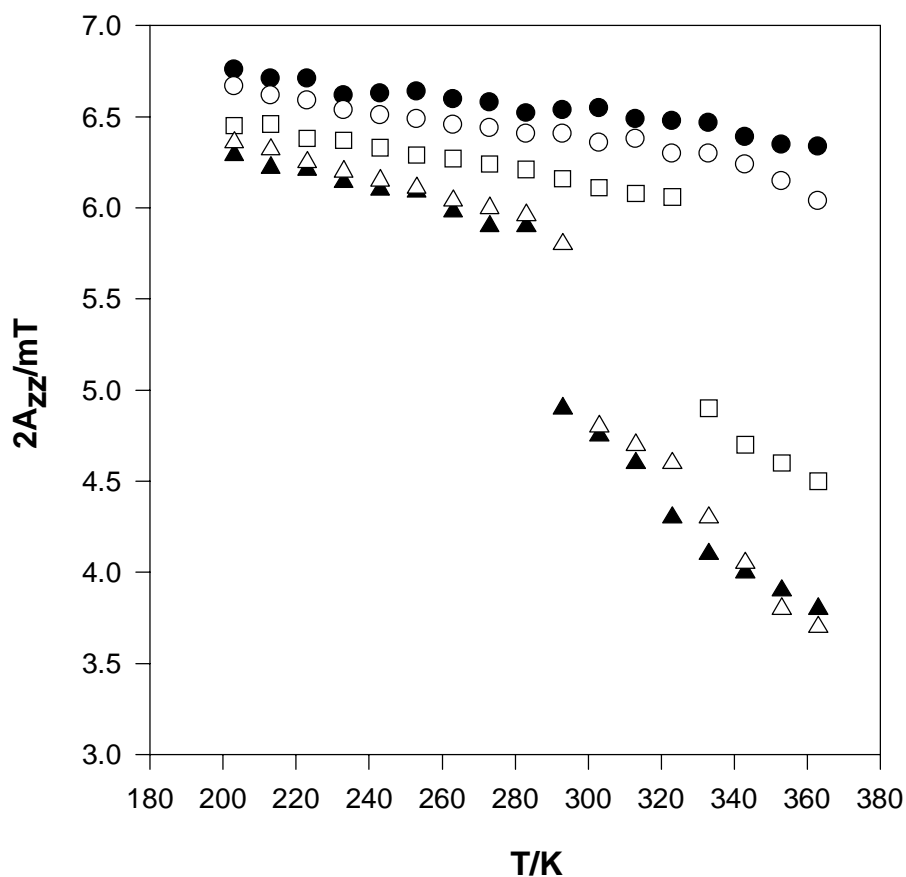
characteristics of probe molecules in a given environment will also depend on the size and shape of a probe [7] due to the fact that the probe motion is associated with the free the free volume in the host matrix. The interaction between probe molecules and polymer chains should also be considered [2]. Therefore, we have used two nitroxyl radicals, Tempo and Tempone. As expected and described in the literature T_{5mT} of PS and statistical copolymers doped with a smaller probe (Figure 2) is shifted to lower temperatures as compared to the T_{5mT} values of a larger probe (Figure 3) embedded in the same matrix. It can be seen tha T_{5mT} decreases with the increasing styrene content in the statistical copolymers, irrespective of a probe molecule used. However, T_{5mT} of both probes embedded in the pure PAN matrix is not yet reached at 380 K. Obviously, molecular motion of probe molecules is highly

restricted due to the PAN chains. The isotactic PAN chains adopt the structure combining roughly 3_1 helical and distorted zig-zag conformers randomly distributed along the chains [8]. Due to the Van der Waals interactions, which are found to be a dominan factor in the chain conformations, the polymer chains are very constrained in the glassy state [9]. Thus, local packing and restricted chain motion will influence the size of "holes" in which a spin probe is located. The largest $2A_{zz}$ values (Figure 2 and Figure 3) or slowest probe motion in PAN matrix confirm very dense packing or smaller free volume as compared to the PS homopolymer matrix. Atactic polystyrene is amorphous without an indication of local ordering as seen in PAN [10]. Therefore, continuous narrowing of the outer maxima below T_g, with an increase of the polystyrene component is reasonable. One can also expect that the probe with a hydroxyl group will demonstrate a stronger interaction with the very polar PAN chains as compared with the probe without a functional group. This effect can also contribute to the T_{5mT} shifts.

According to the DSC measurements T_g values of PS and PAN are very close [11]. The same is valid for T_g of SAN-90S and PAN (369.0 and 363.6 K, respectively). In contrast to the DSC results, T_{5mT} reveal considerable difference between these two pairs of polymers. Obviously, the spin probes distinguish the local environment or free volume in the given copolymers, whereas T_g determined by means of DSC measurements reflects the large scale segmental motions.

Except the shifts in T_{5mT} of copolymers with the same monomer pair, but of different composition, the ESR line shape above the glass transition temperature gives additional insight into the microheterogeneity. The SAN-10S copolymer shows a composite spectrum (Figure 4a). The superposition of a slow (s) and fast (f) component in the spectrum above T_{5mT} is interpreted as the existence of two noninterconverting spi populations. A very small population of probes in the fast component is attributed to the domains with larger free volume. The slow component, which remains present above T_{5mT}, is ascribed to the regions with restricted motions. Since th homopolymers of polystyrene and polyacrylonitrile are immiscible, the fast component of the spectru
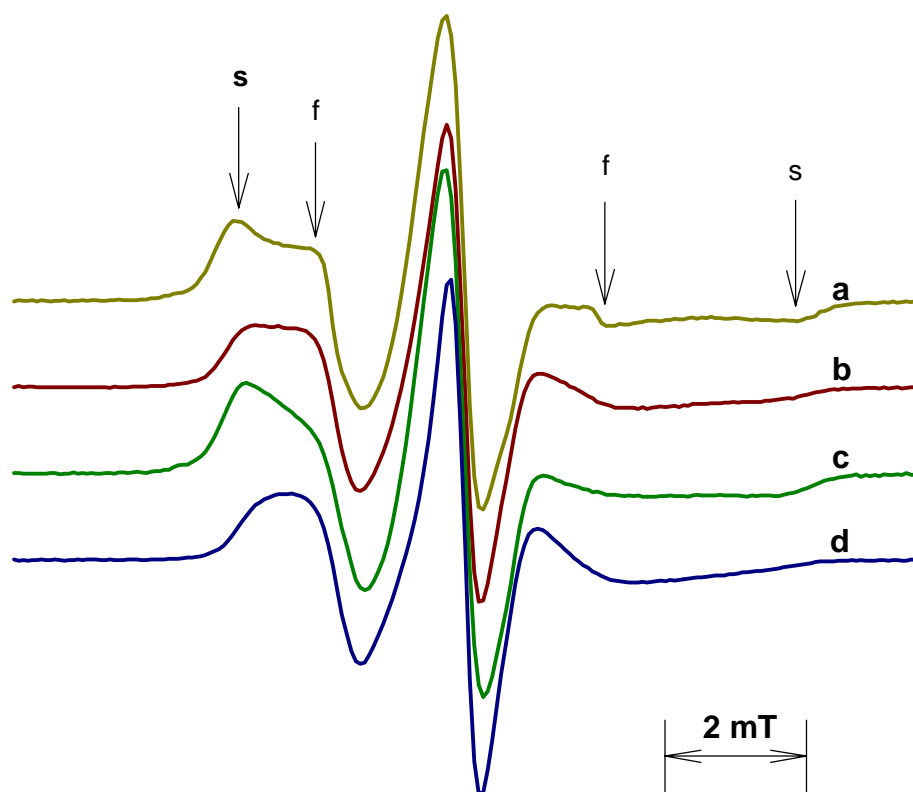
Figure 4. ESR spectra of SAN-10S (a), SAN-54S (b), SAN-49A (c) and SAN-90S (d) doped with Tempone at 353 K.

presumably corresponds to the locally separated styrene sequences in the statistica copolymer. In the case of copolymer having only 10% o acrylonitrile component the ESR spectrum is dominated by the polystyrene fast component (Figure 4d). The simulation of the experimental spectra with the pure PS and PAN component shows that at higher temperatures (above T_{5mT}) the population of spin probes in the acrylonitrile phase decreases at the expense of the polystyrene component. This has been also confirmed by the experiment in which PS and PAN were separately spin probed with the same probe concentration and then mixed in 50:50 molar ratio. The ESR spectra of the mixture simulated with the pure PS and PAN components have confirmed a slight diffusion of a

probe in the polystyrene phase at higher temperatures. This can be explained with the fact that the spin probe is located in the regions with the greatest free volume in the bulk [12]. Since the generation of free volume in polystyrene phase is faster with increasing temperature, this may be expected. On the other hand the concentration of spin probe in a given phase will also be determined in part by its relative affinity for a polymer [13]. On the given grounds one can explain why the initial concentration of probes in the copolymer is slightly smaller in the polyacrylonitrile phase as shown from the spectral simulation.
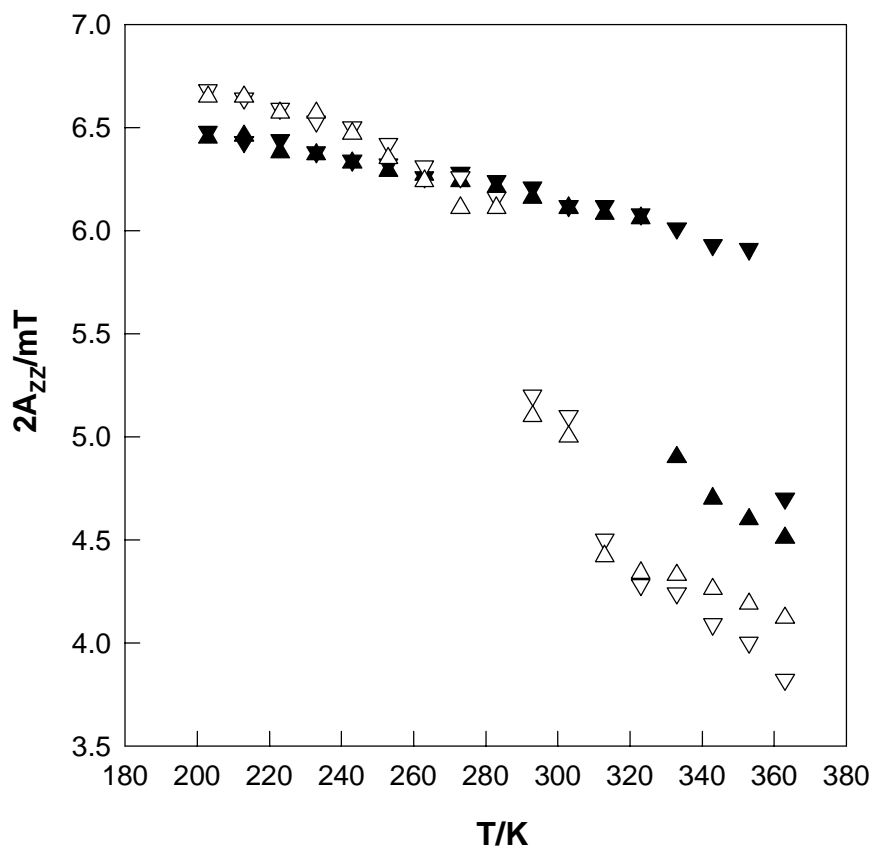

Figure 5. Temperature dependence of the maxima separation ($2A_{zz}$) for samples: SAN-54S (^{a}) and SAN-49A ($\ll$) probed with Tempo and Tempone (filled symbols).

When the larger probe (Tempone) is applied to the SAN-49A and SAN-54S copolymers, T_{5mT} of alternating copolymer is shifted for about 20 K to higher temperatures

as compared to the statistical one (Figure 5). The T_g values determined by means of DSC measurements are 381.0 K and 374.1 K for SAN-49A and SAN-54S, respectively. It has already been confirmed that the sequence distribution of acrylonitrile copolymer has an effect on the glass transition temperature [14]. This fact is explained by the steric and polar interactions between the adjacen monomeric units. Larger shift in T_{5mT} value of SAN-49A to higher temperature are justified with the different microdistribution of styrene rich sequences and the formation of microdomains. The styrene sequences in alternating copolymer contain only of about 20% styrene centered heterotactic triads (SSA), whereas the styrene sequences in statistical copolymer consist of about 55% styrene rich triads (SSA and SSS) as shown from the NMR spectra [15]. At temperatures above T_g the spin probe motion is controlled by the segmental motion which is a small-scale motion with dimensi comparable to those of the probe molecule [2]. Furthermore, on the basis of quantum mechanical calculation [16] and experimenta results [17] it is reasonable to expect that a few bonds along the chain will influence spin probe motion. Therefore, we may conclude that a few local segments or styrene rich domains in SAN-54S will contribute to the faster probe motion or increased free volume. In the alternating copolymer segmental distribution will originate different local polar interactions within the chain and between the chains and, consequently, different local packing and free volume. Thus, T_{5mT} will be considerably lower as compared to the T_{5mT} of SAN-49A.

The size of a Tempo probe is too small as compared to the activation volume at T_g [10] to sense the differences in local packing density. Presented results have shown that the adequately chosen spin probe may successfully be applied to explore the local segmenta packing and the formation of motionally different domains in statistical copolymers. This is possible even if the homopolymer pairs have very similar T_g, but differ in the polar and packing features, which is not accessible by the DSC measurements.

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POVZETE

Molekularno gibljivost in heterogenost statističnih in alternirajočih kopolimerov stirena in akrilonitrila smo študirali v širokem temperaturnem območju z ESR spektroskopijo z uporabo dveh nitroksilnih radikalov, Tempo in Tempone. Temperatura, pri kateri je ločitev zunanjih maksimumov enaka 5 mT, pada z naraščajočo vsebnostjo stirena. Pri kopolimerih z manjšo količino stirena je pri temperaturah nad temperaturo steklastega prehoda nakazana heterogenost v gibljivosti. Razlike v gibljivosti statističnih in alternirajočih kopolimerov podobne sestave smo pojasnili s sekvenčno strukturo polimernih verig. Segmentno urejanje in nastajanje področij z različno gibljivostjo lahko raziskujemo z ustrezno izbranim spinskim označevalcem tudi v primerih, ko imajo homopolimeri zelo podobno temperaturo steklastega prehoda, razlikujejo pa se v polarnosti in urejenosti.