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An electron spin resonance study of molecular dynamics and heterogeneity in the styrene–acrylonitrile copolymers

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Abstract

The spin-probed copolymers of styrene and acrylonitrile differing in monomer content and chain structure were examined by the electron spin resonance (e.s.r.) methods in a wide temperature range. The measurements of spin–lattice relaxation time, T_1^{DM}, in slow motional region by the double modulation e.s.r. technique reveal two distinct relaxation regions in copolymers and pure polyacrylonitrile matrices. At very low temperatures (region I) a very distinct difference between T_1^{DM} values of pure polyacrylonitrile, alternating and statistical copolymers and polystyrene-rich copolymer is ascribed to the effect of packing density of polymer chains. The density modulates the electron spin–lattice relaxation rates and other vibrational modes contributing to the total relaxation rate. At higher temperatures (region II), where the skeleton of a spin probe begins to move, alternating and statistical copolymers of a similar composition show different relaxation rate. The data are reconciled on the basis of the sequence structure of copolymer chains. The difference in glass transition temperature between alternating and statistical copolymers as determined by the e.s.r. measurements reflects local motional heterogeneity as a consequence of chain microstructure. The presence of local motional heterogeneity of a probe near and above the glass transition results from the styrene-rich sequences contributing to the structural heterogeneity in statistical copolymer. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Copolymers of styrene and acrylonitrile have been widely studied as a very interesting material used in many applications due to the excellent balance of physical and chemical properties. An acrylonitrile component imparts some important properties such as toughness, rigidity and resistance to chemicals, due to the strong steric and dipolar forces between adjacent nitrile groups [1]. However, the packing details or morphology and segmental mobility of copolymers differing in the copolymer composition still remains unclear. It is known that the difference of free volume generation with temperature is due to a different packing efficiency and segmental dynamics [2]. The interactions of nitrile groups in the acrylonitrile component as a dominant factor in the chain conformations will certainly contribute to the foregoing characteristics.

One of the methods which can offer an insight into molecular packing on a segmental scale (5 nm) is electron spin resonance (e.s.r.) using nitroxyl spin probes as molecular reporters. The spin probe method is proved to be sensitive to local morphology and segmental dynamics [3]. By measuring electron spin relaxation times, the sensitivity of the continuous wave (c.w.) e.s.r. method to the spin probe motions with rotational correlation times in the range from 10^{-7} to 10^{-11} s is extended from 10^{-6} to 10^{-3} s [4]. Electron spin relaxation times can be very sensitive to slow motional dynamics at low temperatures where the spin probe dynamics is assumed to be nearly rigid. At these temperatures one assumes that the intermolecular and intramolecular solid state relaxation processes will affect electron spin–lattice relaxation time, T_1, spin–spin relaxation time, T_2, or some other relaxation time of a probe. Since in the slow motion regime the homogeneous linewidth ($1/T_2$) of a spin probe is larger than $1/T_1$, it can be expected that the measurements of T_1 would make it possible to reach the smallest detectable effects (approximately the same order of magnitude as $1/T_1$) in the vicinity of a probe [5]. Therefore, to gain more information from intramolecular and intermolecular relaxation processes one can also employ different techniques, such as simultaneous combination of pulsed SR-e.s.r. and electron–electron double resonance,

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ELDOR [6], or two-dimensional ELDOR [7], which may better couple these effects due to the contribution of the electron–nuclear dipolar (END) relaxation rate. A double modulated e.s.r. (DM-e.s.r.) method is used as an alternative method for detecting T_1 of an inhomogeneously broadened line under the condition that $T_1 \gg T_2$ [8–11]. A temperature dependence of the effective relaxation rates can be used to understand the local segmental dynamics, mostly originated from the side chain groups motion and the molecular packing of polymer chains [12]. The faster molecular dynamics near or above the glass transition temperature, T_g, is determined from the temperature sensitive c.w. e.s.r. spectra [3].

The aim of this study is to find out the effect of copolymer chain structure on the chain mobility in a wide temperature range. Special attention is focused on the existence of different local packing density and the segmental motion or generation of free volume in alternating and random copolymers having similar molar ratio of acrylonitrile and styrene monomer units. The degree of spin probe motion depends not only on the free volume generation but also on the probe size and nature, which may cause probe-polymer secondary interactions. The size of a probe is chosen to scan a narrow environmental range. The results of spin probe motional changes in the two copolymers will be compared with the d.s.c. measurements.

2. Experimental

2.1. Sample preparation and characterization

Both homopolymers of polyacrylonitrile (PAN) and statistical copolymers of styrene–acrylonitrile containing 54 (SAN-54S) and 90 (SAN-90S) mol% of styrene were prepared by radical solution polymerization in the batch isothermal reactor with 250 cm^3 of total volume using *N*,*N*-dimethylformamide (DMF, Merck) as a solvent. Monomer components of styrene (INA-OKI, Zagreb, Croatia) and acrylonitrile (OHIS, Skopje, Macedonia) were distilled under the reduced pressure. The reaction mixture was heated to 333 K and the initiator azobisisobutyronitrile (AIBN, AKZO Chemie, The Netherlands) was added in the concentration of 0.01 dm^3. The reaction mixture was constantly nitrogen stirred. The polymer was precipitated in cold methanol and purified by dissolution in DMF and reprecipitated in methanol.

The alternating copolymer styrene–acrylonitrile containing 49 mol% of styrene (SAN-49A) was synthesized in bulk using $ZnCl_2$ as a complexing agent at a reaction temperature of 313 K [13]. The molecular weights of all the samples, as determined by g.p.c. and/or diluted solution viscometry, are between 8×10^4 and 3×10^5; the composition of copolymers was determined by the ‘micro-Dumas’ method for the determination of nitrogen content in organic matter. The statistical and alternating SAN copolymers with approximately 50 mol% of styrene contain about 36% and 12% of heterotactic copolymer units (SSA and AAS), respectively, as calculated from the ^{13}C n.m.r. spectra [14].

2.2. Spin probes

2.2.1. DM-e.s.r. measurements

The polymers were doped with perdeuterated spin probe, 4-oxo-2,2,6,6-tetramethyl-1-piperidinyl-oxy (PD-Tempone) in tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) solution in the case of polyacrylonitrile. The solvent was slowly evaporated at 313 K and the samples were further annealed under vacuum near the glass transition temperature for 3 days. The perdeuterated spin probe was used in order to avoid internal motional dynamics of spin probe methyl groups in the slow motion region. Thus, the other relaxation processes characteristic for the polymer matrix can be detected.

2.2.2. C.w. e.s.r. measurements

Nondeuterated spin probes 4-oxo-2,2,6,6-tetramethyl-1-piperidinyl-oxy (Tempone) and 2,2,6,6-tetramethyl-1-piperidinyl-oxy (Tempo) were used. The concentration of spin probes was less than 0.02 mass%.

2.3. Measurements of the spectra

The c.w. e.s.r. spectra were recorded on a Varian E-109 x-band spectrometer operating at 100 kHz modulation. DM-e.s.r. spectra were recorded on the same spectrometer using 100 kHz modulation of the Zeeman magnetic field as the first modulation. The second modulation (sweeping in the frequency interval from 250 to 350 kHz) was performed by an additional modulation coil and a Wavetek generator as a radiofrequency source. The modulation peak at 300 kHz was detected at a microwave power of less than 1 mW and accumulated in a standard PC computer. The linewidth at half-height of the DM-e.s.r. spectra, Δ_{obs}, is obtained by fitting Lorenzian lineshape to the experimental DM-e.s.r. spectrum. Under the condition that $T_1 \gg T_2$, Δ_{obs} is related to the spin–lattice relaxation time

$$1/\pi\Delta_{obs} = T_1^{DM} \sim T_1 \tag{1}$$

3. Results and discussion

3.1. Molecular motion at low temperatures (DM-e.s.r. measurements)

Previous study of nitroxyl T_1 in glassy solvents in the sub-T_g region by employing saturation recovery technique, SR-e.s.r., shows well defined behaviour of T_1 as a function of temperature ($1/T_1 \propto T^k$, $k = 2.34 \pm 015$) regardless of the matrix [15]. However, in some cases in the sub-T_g region one expects that the effect of intermolecular and intramolecular dynamics takes an important role in the process. As

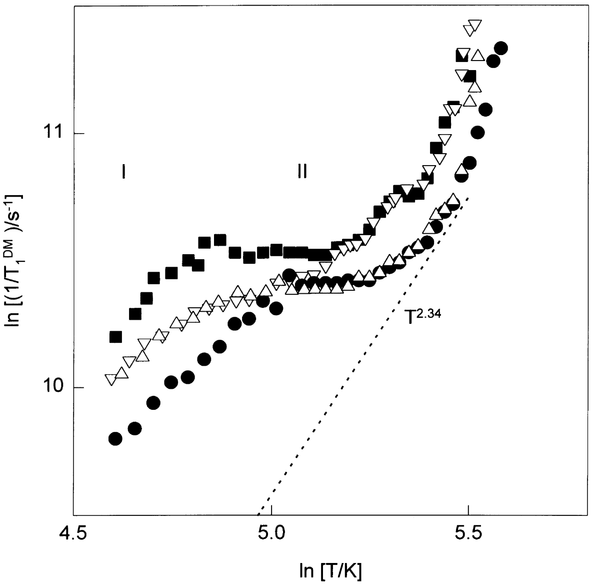

Fig. 1. Log–log presentation of $1/T_1^{DM}$ versus temperature dependence for samples PAN (●); SAN-54S (△); SAN-49A (▽); and SAN-90S (■). The dotted lines represent temperature dependence of $1/T_1^{DM}$ proportional to $T^{2.34}$.

shown earlier, the DM-e.s.r. method can be also employed to detect effect of END relaxation mechanism for the nitroxyl probe in the glassy matrix [12]. The slow molecular motion of perdeuterated spin probe embedded in acrylonitrile–styrene copolymers and polyacrylonitrile homopolymer were measured by the DM-e.s.r. method in the low temperature region from 100 to 250 K, well below the glass transition temperature. The temperature dependence of the DM-e.s.r. linewidths presented as $1/T_1^{DM}$ in a log–log plot is shown in Fig. 1. The dotted line in Fig. 1 represents temperature dependence of $1/T_1$ as $T^{2.34}$, as was expected for the probe in a glassy matrix. Besides a complex temperature behaviour of the $1/T_1^{DM}$, as can be seen in Fig. 1, two distinct relaxation behaviours are generally observed: a low-temperature process (region I, from 100 to 150 K) and a high temperature process (region II, from 200 to 250 K). In region I, relaxation rates for all samples approximately approach the expected coefficient for the spin–lattice relaxation rate in the low-temperature limit. The expected sharp deviation from this coefficient in region II at higher temperatures is also observed. It has been shown in previous papers [16,17] that the change of relaxation mechanism of spin probe in all four samples at about 200 K is connected with the spin probe internal transition.

At very low temperatures (region I) the spin probe is nearly rigid and smaller changes in T_1^{DM} with increasing temperature are detected. However, there is a very distinct difference between T_1^{DM} values of pure polyacrylonitrile and the polystyrene-rich copolymer. At these temperatures all the polymers are well below the glass transition temperature, where the polymer backbone motion is highly restricted [2]. The probe motion in this case is determined by the static free volume and by the local dynamics of side chain groups which are motionally active at low temperatures. Recent experiments have shown that the proton dynamics from the side chain groups modulate the electron-spin–lattice relaxation rate of the probe in the glassy polymer matrix [12]. The longest relaxation time T_1^{DM} of a PAN polymer (Fig. 1) could be explained by the very stiff polymer chains as a consequence of dominant interactions of nitrile groups along the chains and between the chains. An earlier study, using molecular mechanics and molecular dynamics methods of PAN chain conformations, has shown that the atactic PAN chains would adopt the structure combining roughly 3_1 helical and distorted zigzag conformers, randomly distributed along the chains [18]. The Van der Waals interactions were found to be a dominant factor in the chain conformation. Due to these interactions, the polymer chains are very constrained in the glassy state. On the other hand, the spin probes in the polystyrene-rich copolymer exhibit the shortest relaxation time. An increase of the relaxation rate for this polymer is related to the increase in the local density of vibrational states in the glassy matrix, which can be ascribed to the phenyl side chain groups. Flipping of a phenyl ring, as restricted rotation, may introduce some distortion of the matrix [19]. Ring flips require flexibility of a few main chain sites allowing spin probe molecules to increase local mobility. This kind of motion is mechanically active in polystyrene at 153 K [20].

Random and alternating acrylonitrile–styrene copolymers having similar molar ratio of monomer components show the same relaxation rate at very low temperatures. Obviously, at these temperatures, where the spin probe is nearly rigid, the difference in sequence structure of those copolymers does not influence the relaxation rate. Thus, the relative concentration of phenyl side chains promoting additional free volume for the spin probe seems to be the determining factor. However, as the temperature is approaching 150 K the relaxation rates begin to differ. It is known that the relaxation mechanism depends on the modulation of the END interaction between dispersed radicals and neighbouring magnetic nuclei by tunneling modes or by low-lying vibrational states associated with the excitation of a two-level system, TLS, in the glassy matrix [21–24]. The relaxation process is affected by the number or density of these modes and their distribution. Thus, the difference in the relaxation rates of alternating and statistical copolymer can be related to the unlikeness in the local density of vibrational and TLS states. The statistical copolymer exhibits a relaxation rate very similar to the pure PAN, while the alternating copolymer follows the relaxation behaviour of PS-rich copolymer from 150 to 240 K. The faster relaxation rates of the alternating copolymer are due to the higher local density of vibrational states. Each nitrile group is followed by the phenyl one, thus changing a distribution of local Van der Waals forces and consequently the rigidity or stiffness of the chain and local relaxation modes. The results of relaxation rates of these copolymers (Fig. 2) reveal

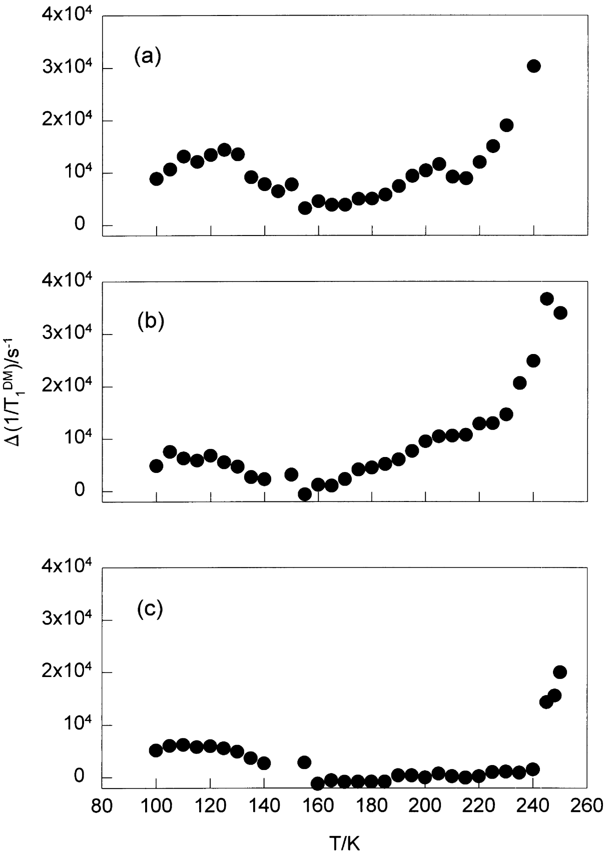

Fig. 2. Temperature dependence of the difference in relaxation rates $(1/T_1^{\mathrm{DM}})$ between: (a) SAN-90S and PAN; (b) SAN-49A and PAN; and (c) SAN-54S and PAN.

the difference in relaxation modes. Fig. 2a shows a contribution of side chain group motion by subtracting relaxation rates of PAN with stiff chain structure from the relaxation rates of PS-rich copolymer. Well-expressed modes at 130 and 220 K are seen. By subtracting the relaxation rates of PAN from alternating copolymer, the same two maxima are still present, but with a lower intensity. However, by the same substraction from the statistical copolymer these modes are not present. In spite of the similar amount of phenyl groups in the statistical copolymer in comparison with the alternating one, the relaxation rates of statistical copolymer seem to be dominated by the slower relaxation modes which originate from the stiffer acrylonitrile sequences.

3.2. Faster molecular motion (c.w. e.s.r. measurements)

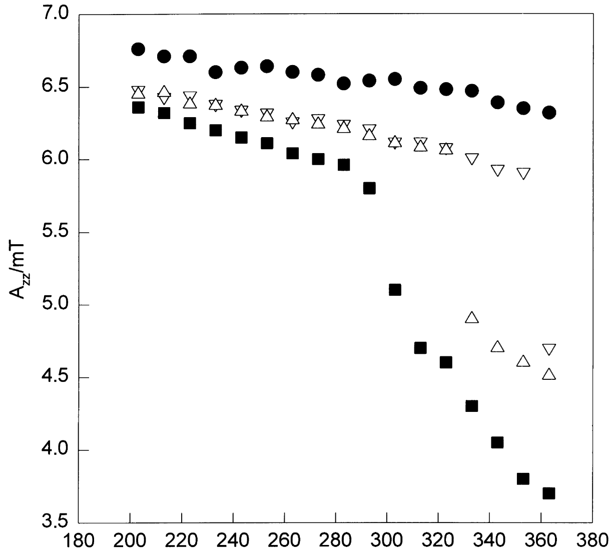

Fig. 3. Temperature dependence of the outer hyperfine extrema ($2A_{zz}$) for samples: PAN (●); SAN-54S (△); SAN-49A (▽); and SAN-90S (■) probed with Tempone.

Of particular interest in the present article is the region at and above the glass transition temperature where the motional behaviour of spin probes is predominantly influenced by the larger free volume changes. In order to compare the molecular mobility of spin probes in homopolymers and copolymers, the outer maxima separation, $2A_{zz}$, of the e.s.r. spectra as a semiquantitative parameter is plotted versus temperature (Figs 3 and 4). A typical sigmoidal curves of $2A_{zz}$ versus temperature at $T_{5\mathrm{mT}}$ are empirically correlated with the glass transition temperature [25,26]. The $T_{5\mathrm{mT}}$ is the temperature at which the outer maxima separation ($2A_{zz}$) becomes $T_{5\mathrm{mT}}$. It is well known that the $T_{5\mathrm{mT}}$ value for a particular polymer depends on the molecular size of a spin probe [27] since the probe mobility is associated with the free volume in the host matrix. For a comparison we have used two spin probes differing in molecular size: Tempone (Fig. 3) and Tempo (Fig. 4). According to $2A_{zz}$ values at lower temperatures (below T_g), both spin probes dispersed in PAN exhibit the slowest mobility

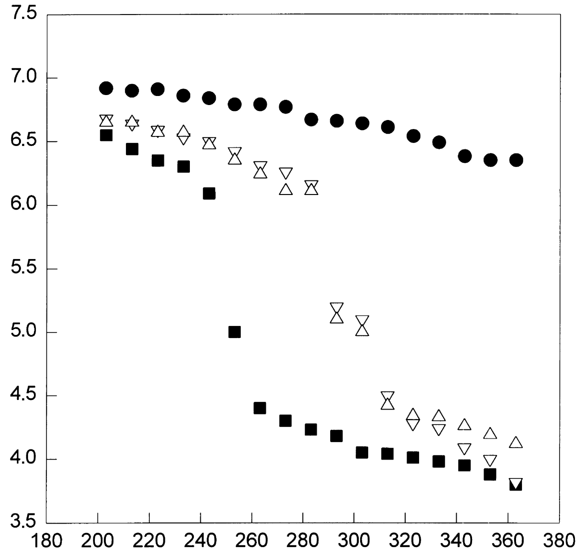

Fig. 4. Temperature dependence of the outer hyperfine extrema ($2A_{zz}$) for samples: PAN (●); SAN-54S (△); SAN-49A (▽); and SAN-90S (■) probed with Tempo.

compared to the probe motion in polystyrene-rich copolymer and two other investigated copolymers, respectively. Those results are in accordance with the T_1^{DM} measurements. The rotation of spin probes in the low-temperature region is predominantly determined by the static free volume [28]. This means that the molecular tumbling of a given probe depends mainly on the size of the ‘hole’ in which it is located. Dimensions of the ‘holes’ will depend on the molecular packing. It should be noted that, at temperatures below T_g, there is no difference in $2A_{zz}$ between the two samples, within the error of measurements, between alternating and statistical copolymer, which is found by using the DM-e.s.r. method. The outer maxima separation does not reveal small differences in the specific local packing. The reason is an insensitivity of inhomogeneously broadened c.w. e.s.r. spectra to slow molecular dynamics.

However, at temperatures at and above T_g, the spin probe motion is controlled by segmental motion of polymers, which is the small-scale molecular motion with dimensions comparable to those of the spin probe. Therefore, T_{5mT} reflects the microenvironment around the probe molecules, while T_g determined by means of d.s.c. corresponds to the larger scale of segmental motion. T_{5mT} of polystyrene-rich copolymer is considerably lower than T_{5mT} of pure PAN, which is not yet reached at 380 K (Fig. 3). The same is valid for the smaller probe (Fig. 4). However, T_{5mT} of SAN-90S is even shifted to lower temperatures, from 300 to 250 K, as expected due to the probe of a smaller molecular size [25].

According to d.s.c. measurements, T_g values of SAN-90S and PAN are very close: 369.0 and 363.6 K, respectively. Due to the e.s.r. results there is a considerable difference between the spin probe motion and free volume generation with temperature between these two polymers. In the case of PAN, the interaction of spin probe and the very polar polymer chains can be expected. The probe with a carbonyl group is expected to demonstrate a stronger interaction than the probe without a functional group. However, T_{5mT} for a smaller probe is not yet reached at 380 K. Obviously, the main chain stiffness and local packing has a predominant influence on spin probe motion. Certain local ordering, which has not been found in SAN-90S samples, is confirmed by X-ray measurements. Though the PAN is a mainly atactic polymer, the local distribution of microstructural units could induce local crystallization. A very small contribution of crystalline domains is controlled by the polymer microtacticity [29]. However, both copolymers SAN-49A and SAN-54S are predominantly disordered due to the X-ray diffractograms. There is only a very small indication of the beginning of ordering.

The T_{5mT} values of both SAN-49A and SAN-54S are placed between polystyrene-rich copolymer and PAN (Figs 3 and 4). If the larger probe is applied, the T_{5mT} of SAN-49A is shifted for about 20 K to higher temperatures as compared to SAN-54S. Again the motional difference expressed as T_{5mT} between the two copolymers is larger than the difference between T_g values determined by means of d.s.c. (381.0 and 374.1 K for SAN-49A and SAN-54S, respectively). The effect of the sequence distribution of acrylonitrile copolymers on the glass transition temperature has been established [30]. It is mainly due to steric and polar interactions between adjacent monomeric units. Moreover, it has been shown elsewhere [31] that the dependence of the T_g of the investigated copolymer on the copolymer composition may be approximated by Barton’s equation [32], which is derived on the postulates of sequence distribution calculations. Therefore, T_{5mT} values of SAN-49A and SAN-54S (Fig. 3) can be explained by the different micro-distribution of styrene sequences and the formation of micro-domains. The styrene sequences in alternating copolymer consist only of about 20% styrene centred heterotactic triads (SSA), while the styrene sequences in statistical copolymer contain about 55% styrene-rich triads (SSA and SSS). It has been suggested [33], and confirmed theoretically using ab initio quantum mechanical calculations [34], that it is unlikely that the motion responsible for the probe or label rotation extends more than a few bonds along the main chain. Therefore, we may conclude that a few local chains with styrene-rich sequences (domains in SAN-54S) surrounding the probe molecule contribute to faster local generation of free volume, and thus to faster motion of spin probes. In the case of alternating copolymer, polar interaction within the chain and between the chains induce different local segmental motion which will be sensed by the spin probe. In the case of smaller spin probe, the size of a probe seems to be too small as compared to the activation volume at T_g of the polymer [28]. Sequence distribution was found to affect the other properties as well, such as miscibility behaviour of copolymer mixtures [35,36]. Homotactic, heterotactic and alternating triads were found to interact in different a manner with each other, as quantified by different values of interaction parameters, χ. Thus, packing of segments and even the formation of microdomains may be expected in random copolymers, which can change the local free volume generation with temperature and consequently the spin probe dynamics.

Lineshape analysis would certainly give more information on motional dynamics in alternating and statistical copolymers. However, in this case the problem of anisotropic motion must be considered in terms of polar environment introduced by acrylate units. Since the two copolymers differ in the microstructure of the copolymer chain, as well as in the sequence distribution within the chain, as shown by n.m.r., it is difficult to predict the simulation parameters which would exactly describe the type of anisotropic motion. Furthermore, a distribution of rotational correlation times caused by the variation in the local structure will introduce additional uncertainty in the spectral simulation. Thus, one can rely only on the semiquantitative results such as $2A_{zz}$. In the case of a very small spin probe, the $2A_{zz}$ appears to be similar for all the samples. However, the linewidths at temperatures above T_g (Fig. 5) are not affected in

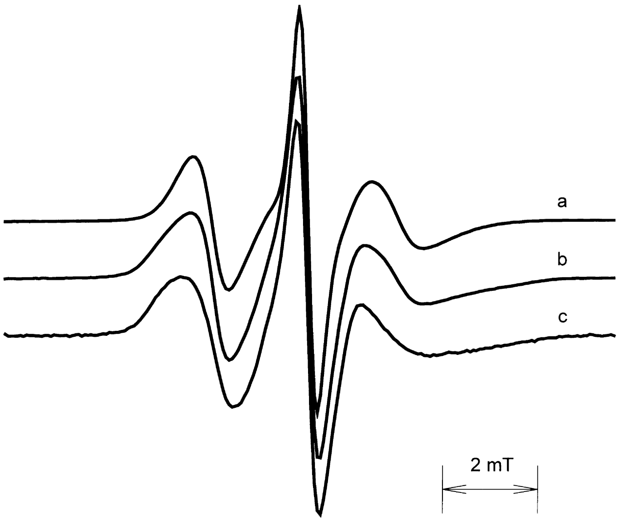

Fig. 5. C.w. e.s.r. spectra of (a) SAN-90S; (b) SAN-49A; and (c) SAN-54S probed with Tempo at 363 K.

the same way by the increase of temperature. The larger half-width at half-height of low- and high-field extrema in SAN-54S compared to SAN-49A can be ascribed to a more heterogeneous environment [37,38] caused by the sequence structure.

4. Conclusions

The spin-probed styrene–acrylonitrile copolymers were measured by employing double modulated e.s.r. and c.w. e.s.r. covering a wide range of molecular dynamics. The DM-e.s.r. technique extends the range of experimental information due to the ability of nitroxyl radical to couple protons in the matrix and possible low-lying excitation levels of the matrix. It is shown that the effective relaxation rates of the probe can be used to elucidate local molecular dynamics and molecular packing due to the polymer sequence structure. The analysis of alternating and statistic copolymers of a similar composition just above the glass transition temperature (c.w. e.s.r.) also reveals that local structural heterogeneity, introduced by the sequence structure, is reflected in the probe dynamics and $T_{5\mathrm{mT}}$ parameter.

Acknowledgements

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