

**Spin Label Studies  
of Poly(phenylvinyl alkyl thioethers)-co-Maleic Anhydride  
in Different Solvents**

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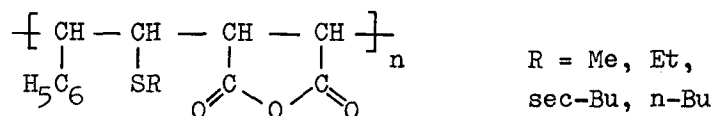
*Dedicated to Prof. Dragutin Fleš in honor of his 60th birthday*

SUMMARY

Alternating copolymers of poly(phenylvinyl alkyl thioethers) and maleic anhydride covalently labeled with 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl and 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl free radicals in different solvents were investigated. The alkyl groups were Me, Et, sec-Bu and n-Bu. The rotational correlation times,  $\tau_R$ , characterizing the rate of rotation of spin label, are not significantly affected by the alkyl group at low solvent concentration. However, at higher dilution (above  $T_g$ )  $\tau_R$  is increasing with the increased bulkiness of the alkyl group. The motion of the two spin labels attached to the copolymer segment through different chemical linkage and an implication on the effective correlation time was discussed.

INTRODUCTION

Alternating copolymers of poly(phenylvinyl alkyl thioethers) and maleic anhydride represent a special class of regular polymers (KUREŠEVIĆ et al. 1979, VUKOVIĆ et



al. 1979) where alkyl group R could be varied. Generally very little is known about the solvent-polymer

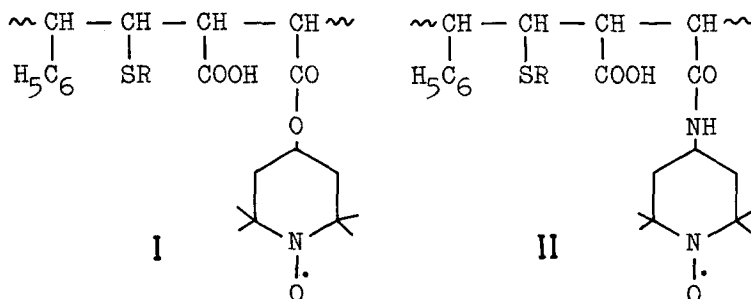
interaction in this type of polymers. However, the interaction of these copolymers with different solvents or plasticizers is of the special interest concerning their application as additives in the petroleum and petrochemical industry.

In the present communication we attempt to present some of the results of copolymer-solvent system deduced by the spin labeling technique. This technique has proved useful for elucidation of the nitroxide motion as a function of solvent composition (BULLOCK et al. 1973, WEE and MILLER 1973, MURAKAMI et al. 1976, VEKSLI and MILLER 1977a, 1977b). The ESR spectra of nitroxide radicals bound to the copolymer provide information on the way in which the reorientation of nitroxide, characterized by a solvent concentration dependent rotational correlation time ( $\tau_R$ ) is affected by the bulkiness of alkyl group and the nature of solvents. The alkyl group R in the thioether moiety was Me, Et, sec-Bu and n-Bu respectively.

Two types of spin labels of the same volume but different functional groups were used in order to study the influence of attachment on the internal rotation of nitroxide and on effective solvent concentration dependent correlation time.

#### EXPERIMENTAL

Nitroxide labels were randomly covalently attached to



the anhydride group in the copolymer chain: 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl through ester linkage(I) and 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl through amide linkage(II).

The labeling procedure was carried out in methyl ethyl ketone (MEK) at 60°C. Labeled copolymers were precipitated with cold n-heptane or dimethylether depending on the alkyl group R. The molecular weights of copolymers were between 5000 and 10000.

ESR spectra were measured on a Varian E-109 spectrometer with 100 kHz modulation (modulation amplitude less than 0,1 mT).

Glass transition temperatures( $T_g$ ) were determined with Perkin-Elmer differential scanning calorimeter model DSC-2.

#### RESULTS AND DISCUSSION

The ESR spectra of the copolymers were measured as a function of the solvent concentration at room temperature. Addition of thermodynamically good solvents like MEK or acetone to the labeled copolymer affects the nitroxide motion in a similar manner (Fig. 1) irrespective of the type of the label attached.

Small amounts of a solvent change the motion very slightly until a critical concentration is reached. The concentration, responsible for an appearance of the motionally narrowed spectra is connected with the glass transition temperature lowering to the temperature of ESR measurements. The copolymers studied have glass transition temperature in the range from 220° to 230°C depending on the alkyl group in the thioether moiety. DSC measurements have shown that the critical concentration of MEK which lowers  $T_g$  to the temperature of ESR measurements is rather low; between 20 to 35 wt % of MEK depending on the bulkiness of alkyl group.

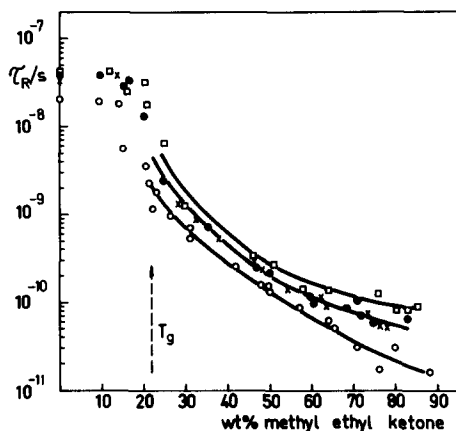


Figure 1. The concentration dependence of the rotational correlation times of the labeled copolymers(I): R=Me(O), R=Et(●), R=sec-Bu(x) and R=n-Bu(□).

As can be seen in Fig. 1. the solvent concentration rapidly changing the rotational correlation time coincides with the DSC measurements.

The interpretation of the ESR spectra relied on the rotational correlation time calculation from approximate relationships but not from a complete line shape analysis which has been adequately reviewed (BERLINER 1976). The correlation times were determined from the extrema separation using slow motion theory (GOLDMAN et al. 1972, MASON et al. 1974) and from the three component spectra in the motional narrowing region (KIVELSON 1960, BULLOCK 1976). Though calculated values of  $\tau_R$  are only approximative, the qualitative features of  $\tau_R$  vs solvent concentration curves are unchanged.

As can be seen in Fig. 1. the correlation times above  $T_g$ , in the motional narrowing region, depend on the alkyl group present. With an increasing bulkiness of alkyl group the motion of nitroxide is slower. Above the

glass transition the difference in  $\tau_R$  imparted by the alkyl group is negligible. As the nitroxide is bound by a side chain to rather immobile polymer segment in the low solvent concentration range, it follows that the nitroxide rotation is determined by the side chain motion. However, at higher dilution (above  $T_g$ ) at least two motions affecting nitroxide motion should be considered: the side chain rotation and local segmental backbone motion (VASSERMAN et al. 1981). It is reasonable to expect that side chain rotation in all four copolymers is the same. Thus a change in the effective correlation time may be attributed to the steric constraints on the segmental motion imparted by the alkyl group.

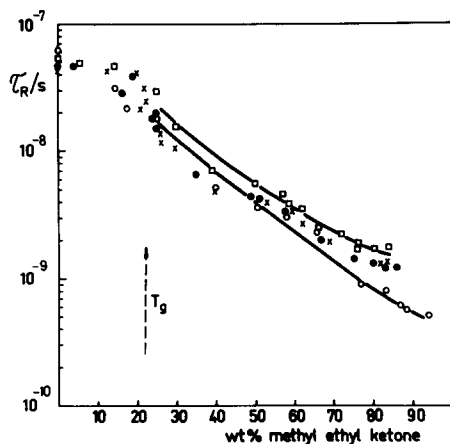


Figure 2. The concentration dependence of the rotational correlation times of the labeled copolymers(II): R=Me(O), R=Et(●), R=sec-Bu(x) and R=n-Bu(□).

Fig. 2. represents the same copolymers in the presence of MEK but labeled through amide linkage. General behaviour of the copolymer-solvent system is similar. There is a difference in the correlation time value. The ESR spectra are highly anisotropic compared to the

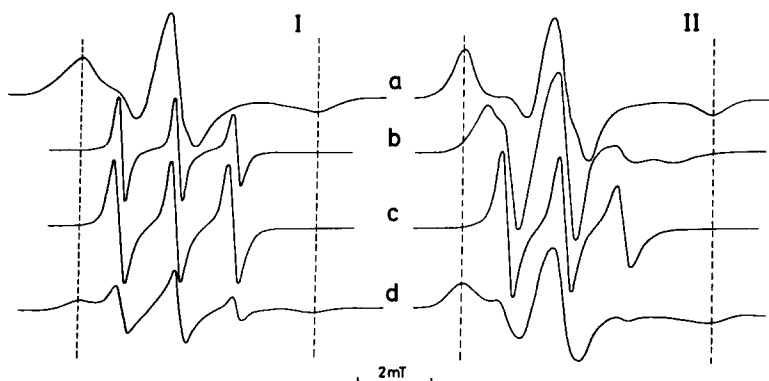


Figure 3. The ESR spectra of the labeled copolymers I and II at room temperature: a) solid copolymer, b) 40 wt % MEK, c) > 80 wt % MEK and d) > 80 wt % benzene.

ESR spectra of labeled copolymer through ester linkage (Fig. 3). A reason is probably the presence of the amide linkage ( $-\text{CO}-\text{NH}-$ ) which is regarded as rigid and represents a stronger hindering factor than the ester linkage (WALLACH 1967, PILAR et al. 1979). There is also a possibility of internal hydrogen bonding which may contribute to the restriction of side chain rotation. Furthermore, the side chain-solvent interaction is not similar in both spin labels.

As the glass transition appears approximately at the same solvent concentration for labeled copolymers I and II respectively, and their side chain motions are different, the similar segmental motion seems to be responsible for  $T_g$ .

Benzene appears to be a bad solvent for copolymers. Even at a very high dilution the ESR spectra show a composed spectrum: a broad component characteristic for the bulk copolymer and motionally narrowed spectrum irrespective of the spin label (Fig. 3). Though benzene and MEK or acetone have similar solubility

parameter the low polarity of benzene seems to be insufficient to reduce interaction opposing copolymer dissolution (MORAWETZ 1975). Therefore an adequate cosolvent of similar boiling point was used. Benzene-MEK 1 to 1 mixture added to copolymers shows qualitatively the same behaviour of nitroxide motion as in the case of pure MEK (Fig. 4)

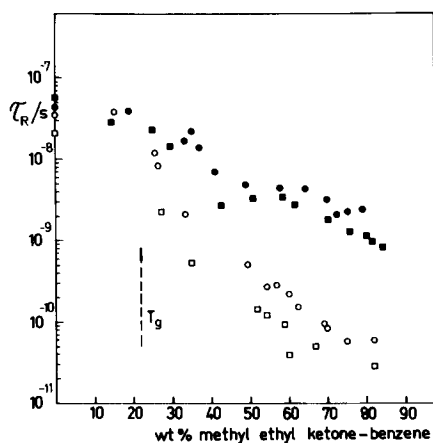


Figure 4. The concentration dependence of the rotational correlation times of the labeled copolymers in mixed solvents: (I) R=Me( $\square$ ), R=sec-Bu( $\circ$ ); (II) R=Me( $\blacksquare$ ) and R=sec-Bu( $\bullet$ ).

Recently VASSERMAN et al.(1981) have shown that the correlation time of segmental motion can be determined from the fast anisotropic spin label rotation, but the model depends on the choice of label.

In order to determine  $\tau_R$  of segmental motions in the copolymers additional measurements are in progress.

#### ACKNOWLEDGEMENT

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