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Concentration Dependence of Local Chain Motions of Polymers

^{13}C-NMR Relaxation of an Alternating 1,4 – trans – Butadiene – Propene Copolymer

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SUMMARY

The chain dynamics of an alternating 1,4-trans-butadiene-propene copolymer has been investigated by high resolution ^{13}C NMR spectroscopy in a broad range of concentrations in solution and in the melt. While in semidilute solution all main chain carbon atoms have the same activation energy of motion it is found that, above a concentration of 20 wt%, the activation energy of the aliphatic carbon atoms increases faster with concentration than the activation energy of the olefinic carbon atoms. It is concluded that in dilute and in semidilute solution all carbon atoms are relaxed by localized transitions about methine-methylene bonds, i. e. the bonds with the lowest energy barrier, whereas in concentrated solution and in the melt the relaxation of aliphatic and olefinic carbon atoms is controlled by independent localized transitions about methylene-methylene and methine-methylene bonds, respectively.

INTRODUCTION

Recently convincing experimental evidence by eximer fluorescence has proven that "crankshaft-like motions" by which conformational transitions in polymers were supposed to occur do not exist in dilute solutions 1). By a recent reaction rate theory of conformational kinetics in dilute solution 2,3), rate constants for conformational transitions could be calculated on the basis of localized transitions about single bonds of the chain backbone in reasonable agreement with experimental values. The theoretical model also dissolves the hitherto existing discrepancy between the low activation energies of motion observed by various experimental methods, e. g. dielectric relaxation 4) and NMR 5), and the higher energies postulated by the assumption of simultanous rotation about a limited number of bonds in a crankshaft-like mechanism. The question remains open, however, if crankshaft-like motions exist in bulk, in the melt or perhaps even in concentrated solutions, where intersegmental restrictions may impede distortions of bond rotational angles in the neighbourhood of a localized single bond transition and favourize correlated rotations. In order to elucidate this question we investigated the ^{13}C NMR relaxation behaviour of an amorphous elastomer, an alternating 1,4-trans-butadiene-propene copolymer, where the spin lattice relaxation times T_1 and the nuclear Overhauser enhancement factors NOEF of five magnetically nonequivalent backbone carbon atoms can be measured over a broad range of concentrations from dilute solution to the melt. A previous ^{13}C relaxation study of this copolymer in the melt gave evidence of two kinds of local conformational transitions 6).

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EXPERIMENTAL

The alternating 1,4-trans-butadiene-propene copolymer sample(M_n = 128 000) was supplied by Marzen Petrochemical Co. Ltd., Tokyo, Japan. The measurements were carried out on a Bruker WH 90 spectrometer at a ^{13}C frequency of 22.63 MHz after purifying the sample by casting several times from THF with methanol.

RESULTS

The temperature dependence of the T_1 and NOEF values of the 5 magnetically nonequivalent carbon atoms of the repeating unit of the copolymer was measured at 5 concentrations(9, 16, 21, 40 and 60 wt%) in $CDCl_3$ solution. The results of the 9% and 60% solution are represented in Fig. 1. For reasons of clarity the T_1 values and not the NT_1 values reduced to one proton interaction are given(N is the number of directly bonded protons) which have to be used for direct comparison.

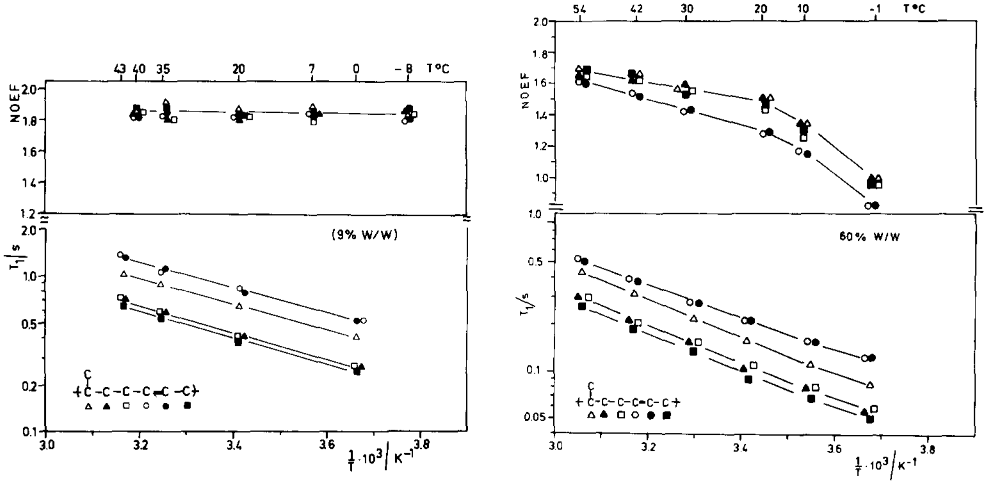

Fig. 1: ^{13}C spin lattice relaxation times T_1 and nuclear Overhauser enhancement factors NOEF of alternating 1,4-trans-butadiene-propene copolymer

At the lowest concentration(9%) all carbon atoms have the same NOEF. A differentiation can be noted, however, between the NT_1 values of the various carbon atoms of the chain backbone.(We don't discuss the trivial case of the methyl group rotation). The lowest NT_1 is exhibited by the tertiary carbon atom (Δ) followed by the methylene carbon atom(■) between the tertiary carbon atom and the double bond. The highest NT_1 is exhibited by the other methylene carbon atoms (▲, □) and the olefimic carbon atoms(O, ●). There is no significant difference between the T_1 values of the olefinic carbon atoms. With increasing concentration the magnitude of T_1 and of the NOEF decreases as a consequence of enhanced restrictions of the segmental motion . As a more important feature one observes an increasing differentiation between the NOEF of the aliphatic and olefinic carbon atoms starting at about 16 wt% as well in magnitude as in the temperature behaviour of these groups. Furthermore a significant decrease of the temperature coefficient of T_1 of the olefinic carbon atoms sets in at about 40%. Both effects are documented for the 60% solution in Fig. 1.

Several models 7,8) based on a three bond jump mechanism on a tetrahedral lattice have been devised by which spin relaxation of polymers with tetrahedral chain geometry could be successfully described in dilute solution.[5] Though the copolymer under investigation does not posses tetrahedral chain geometry the VJGM model [7] was tested and it is possible, in fact, to fit the results in solution and the data of the aliphatic carbon atoms in the melt. The data of the olefinic carbon atoms in the melt at lower temperatures could not be fitted by any reasonable choice of the parameters of the model in consequence of the low NOEF. In view of this fact and the experimental evidence against crankshaft-like motions, as discussed below, we chose a formal distribution function of correlation times of the Cole-Cole type for the description of the relaxation data. The distribution function is characterized by a mean correlation time τ_o and a width parameter γ and has beeen used before in the analysis of ^{13}C relaxation experiments of polymers. Also with this model it is not possible to analyse all data of the olefinic carbon atoms in the melt. This difficulty can be circumvented in principle by introducing an internal correlation time as an additional third parameter [6] by means of which it is also possible to analyse the NT_1 differences between the main chain carbon atoms in terms of different internal correlation times of these atoms. Since in the present discussion we want to put emphasis on the effect of concentration on local chain motions we use the simpler two parameter model.

As has been noted before [6] it is not possible with the two parameter distribution function to decribe the motion of aliphatic and olefinic carbon atoms by the same autocorrelation function, i. e. with the same τ_o and γ-parameters, at higher concentrations where different NOEF values are found for these carbon atoms. The variation of the width parameter γ with temperature and concentration is shown in Fig. 2 . Except for the lowest concentration (not shown) the γ-value of the olefinic carbon atoms is always smaller than the γ parameter of the aliphatic carbon atoms at a given temperature. All aliphatic carbon atoms, however, are characterized by the same width parameter. The distribution of correlation times narrows as indicated by decreasing γ with decreasing concentration in a similar manner as for other systems [5].

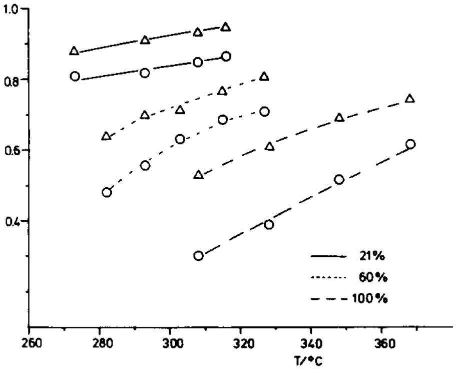

Fig. 2: Width parameter γ of the Cole-Cole distribution function of correlation times of aliphatic(Δ) and olefinic(O) carbon atoms

Fig. 3 snows the variation of the mean correlation time τ_o of propylenic methine and olefinic carbon atoms with temperature and concentration. The τ_o values of the olefinic carbon atoms in the melt are subject to considerable errors because of the critical determination of the γ-parameters and the flatnes of the T_1 vs. τ_o curves in the range of small γ-parameters($\gamma < 0.4$) at lower temperatures. Therefore they have been omitted in Fig. 2. As mentioned above the NT_1 differences between the aliphatic carbon atoms in Fig. 1 can be interpreted in terms of different internal correlation times τ_{ir} at constant τ_o and γ. By setting the ratio $f = \tau_{ir}/\tau_o$ to $f = 1$ for the tertiary propylenic carbon atom as an arbitrary reference one finds that the ratios of the correlation times are $f(CH_2$, ■) = 0.5 and $f(CH_2$, □ , ▲) = 0.35 (for definition of symbols refer

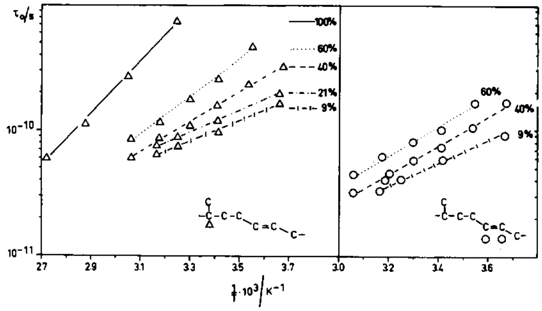

Figure 3: Mean correlation time τ_o of propylenic methine and olefinic carbon atoms

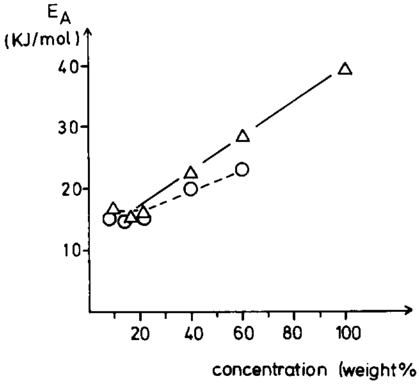

Figure 4: Activation energies as determined from Figure 3

to Figure 1) independent of temperature and concentration. Figure 3 shows that the the temperature coefficient of the mean correlation time of the aliphatic carbon atoms increases more rapidly with concentration than for the olefinic carbon atoms. In Figure 4 the activation energies as determined from Figure 3 are plotted versus concentration. While the same effective barrier of 15 kJ/mol is seen by both the alifatic and olefinic carbon atoms in the range of lower concentrations up to ca 20% an increasing differentiation between the activation energies occurs for both kinds of atoms towards higher concentrations. This is an interesting result because generally the correlation times of all main chain carbon atoms exhibit the same temperature behaviour irrespective of concentration [5]. In an earlier ^{13}C relaxation study of cis-trans-1,4-polybutadiene a cross-over of the T_1 curves of the carbon atoms of cis and trans units had already been observed in the melt[9]. Therefore it appears that the observed differentiation between the effective activation energies of aliphatic and olefinic carbon motion in Figure 4 is a peculiar intramolecular feature related to the presence of the double bonds. Since this differentiation is observed only at concentrations exceeding a certain limiting value also intermolecular effects must play an important role. At sufficiently high concentrations where a uniform segment density is reached one may assume that the microscopic viscosity on a segmental level which governs the rate of conformational transitions is related to the free volume in a similar way as the macroscopic viscosity. According to a treatment of FUJITA [10] which has also been used in the description of dielectric relaxation data [11] the concentration dependence of the mean correlation time τ_o at constant temperature can be expressed as

$$\frac{\Delta\Phi_2}{\ln(\tau_o/\tau_o^*)} = a - b\Delta\Phi_2 \qquad (1)$$

where τ_o^* is the mean correlation time at a reference concentration and a, b are constants depending on the reference concentration at a reference temperature and $\Delta\phi_2$ is the difference between the polymer volume fractions at the actual and the reference concentration. In the range of validiy of the free volume treatment a plot of the l. h. s. of Eq. 1 in dependence on $\Delta\phi_2$ should yield a straight line. Figure 5 shows such a plot for the propylenic and olefinic carbon atoms at two temperatures. The plots are nonlinear. Obviously the assumption of a uniform segment density on a microscopic scale is not achieved throughout the concentration range. The onset of a uniform segment density may roughly be defined as the intersection of a linear approximation of the regions of weak and strong concentration dependence in Figure 5. Comparing with Figure 4 one finds that the transition to a uniform segment density occurs at approximately the same concentration of ca 20% at which the onset of the differentiation between the activation energies of motion of aliphatic and olefinic carbon atoms is observed.

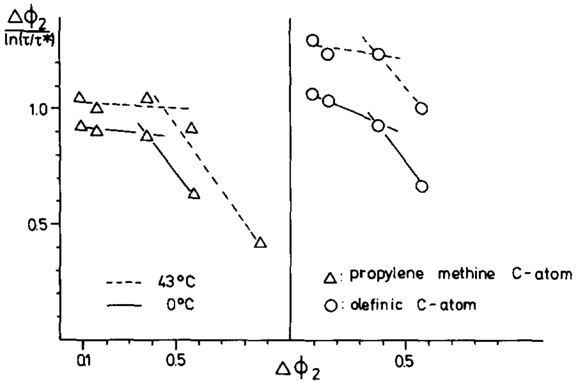

Figure 5: Concentration dependence of correlation times according to Eq. 1

DISCUSSION

1. General features. The mean correlation time of the propylenic carbon atoms is always ca 2 times longer than the mean correlation time of the olefinic carbon atoms throughout the whole range of concentrations. At 9 wt% and 298K, for instance, one finds $\tau_0 = 9\cdot 10^{-11}$s for the propylenic and $\tau_0 = 5\cdot 10^{-11}$ s for the olefinic carbon atoms. On the other hand, the effective rate of motion of the CH_2 groups is estimated to be about 3 times faster than the propylenic and 2 times faster than the olefinic carbon atoms taking the f-values given before. The enhanced rate of motion of the CH_2 groups with respect to the substituted carbon atom and the double bond can be explained by a reduced friction coefficient of the local motions of the former atom groups with respect to the latter ones. A similar behaviour has been found for ethylene-vinylacetate-copolymers [12]. A characteristic feature of the chain dynamics of the present system is that the motions of olefinic and aliphatic carbon atoms are described by two autocorrelation functions of different form characterized by two different width parameters γ in the present analysis with a Cole-Cole distribution function of correlation times unless the solution is sufficiently dilute ($\leq$ 9%). The lower γ-value of the olefinic carbon atoms shows that the motion of these atoms is less isotropic than the motion of the aliphatic carbon atoms. This may be explained by the fact that the loss of orientational freedom about the double bond must lead to a greater anisotropy of reorientation of the CH-vectors of the double bond. Besides the frictional effect also this effect is expected to depress the meancorrelation time of the aliphatic carbon atoms.

2. Concentration effects. In the low concentration region up to 20 wt% a constant common value of about 15 kJ/mol is found for the activation energy of both olefinic and alifatic carbon atoms. This corresponds to a value of only 8 kJ/mol for the intramolecular part of the activation energy if the contribution of the solvent is substracted. This value is of the order of magnitude for a single bond transition about the methine-methylene bond adjacent to a double bond in trans configuration [13]. It is definitely lower than the rotational barrier of ca 12kJ/mol for a single bond transition

about single bonds between methylene groups [13]. Single bond transition behaviour has been found in many dielectric [4] and NMR relaxation experiments [4] of simple polymer systems in dilute solution and theoretical estimates of such transitions have been made recently on the basis of a reaction rate theory [2,3]. The present study shows that in a carbon chain where five single bonds and one double bond in trans configuration are arranged in a regular array the spin relaxation of all carbon atoms in dilute solution is controled by single bond transitions about the bond with the lowest energy barrier, i. e. rotations about the CH_2-CH bonds adjacent to the double bonds . A systematic study in dependence of the number of single bonds between the double bonds and the configuration of the double bond should give more information about the extent of coupling of bonds and the geometrical restrictions involved in these motions. The present study shows that spin relaxation in the lower concentration range ($\leq$ 20 %) is effectuated by coupled motion of at least 6 main chain atoms including the olefinic carbon atoms. Recent calculations suggest that in 1,4-trans-polybutadiene localized transitions centered about single bonds attached to double bonds have a mean transition rate of ca 20 ns^{-1} at 371 K while the mean rate for single bond transitions of the bonds between methylene groups is only 0.4 ns^{-1} [3]. Extrapolating the experimental data of the 9% solution in Figure 3 to 371 K one finds for the mean rate constants of motion of the olefinic and propylenic carbon atoms τ_0^{-1} = 80 ns^{-1} and τ_0^{-1}= 40 ns^{-1} respectively. Taking into account the unknown relation of the local frictional factor used in the calculation to the present experimental conditions and the structural differences both experimental values are in reasonable agreement with the theoretical prediction for the mean transition rate about single bonds adjacent to double bonds. Also this comparison shows that the relaxation of both olefinic and aliphatic carbon atoms in dilute solution is essentially effectuated by single bond transitions about the bonds attached to the double bonds.

The relaxation mechanism is different at concentrations above 20%. If the mean correlation length between intersegmental contacts along the chain becomes smaller than the range of bonds coupled to a single bond transition the local friction coefficient and consequently the correlation time and activation energy of the segmental motion will increase. In a simplified way the motions may be visualized as occuring in different fluctuating environments due to the fluctuating intersegmental contacts. With growing intermolecular restrictions the number of environments will increase in which only one specific local transition about a CH-CH_2, a CH_2-CH_2 bond or no transition at all is possible. Since the lifetime of these environments increases with these restrictions it can be expected that the rate of motion of a given main chain carbon atom within such environments is determined primarily by the rate of motion about the single bonds to which the carbon atom is connected. Therefore it is plausible that in concentrated solution the temperature dependence of the correlation time of a given carbon atom will reflect the characteristic barriers of rotation about the bonds adjacent to the observed carbon atom rather than the influence of bonds farther apart from the carbon atom considered. Transitions of the latter bonds will play a more important role in dilute solution where cooperative motions of larger scale are favourized by energetical and geometrical reasons. Of course, the activation energies derived from the temperature dependence of the mean activation energy in concentrated solution are not only of intramolecular but also of intermolecular origin. Also the difference between the activation energies of olefinic and aliphatic carbon atoms in concentrated solution (s. Figure 4) cannot be interpreted simply as a corresponding difference between intramolecular barriers of specific local transitions. Since this difference increases with concentration different concentration dependent friction coefficients must be associated with these transitions. At a concentration of 60% the observed difference already exceeds the expected difference of ca 4kJ/mol between the local rotational barriers of the two kinds of single bonds of the copolymer. If the data of the olefinic carbon atoms in Figure 4 are extrapolated to the melt where no fit can be obtained with the Cole-Cole distribution function an activation energy of ca 30 kJ/mol is estimated whereas the corresponding value for the propylenic carbon atoms is ca 40 kJ/mol. Assuming additivity of energies the former value is of similar magnitude as the intramolecular energy barrier of two cooperative $s^+Ts^- \rightleftarrows cTc$ conformational transitions ($s^\pm$, c for skew$^\pm$, cis conformations of the $=CH-CH_2$ bond, T for the trans configuration of the CH=CH bond) of the single bonds adjacent to the trans double bonds which are involved in the seven bond crankshaft mechanism proposed in an earlier paper 6) as a possible relaxation mechanism in the melt for the relaxation of the olefinic carbon atoms. The latter value of 40 kJ/mol is of the same order as the intramolecular barrier for three bond motions of the Boyer crankshaft type 14) involving rotations about the five single bonds between the double bonds. This motion represents an efficient relaxation mechanism for the aliphatic carbon atoms. These considerations show that crankshaft mechanisms ruled out for dilute solutions are not likely to occur in the melt either. Otherwise a negligible intermolecular contribution to the energetics of local chain dynamics would have to be assumed in the melt. If crankshaft motions occur in the melt the lowering of the measured activation energies below intramolecular barriers with increasing dilution would imply a rather abrupt transition from a crankshaft like motion with negligible friction effects to a highly damped single bond transition mechanism. This appears to be unlikely since no corresponding abrupt changes is observed in the relaxation behaviour. There are no conceptual difficulties if one assumes that in concentrated solution as well as in the melt spin relaxation proceeds by damped segmental motions localized about single bond transitions.

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