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The transition moment angle of the ν_{CN} vibration in SAN copolymers

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Summary

Fourier transform infrared dichroism was used to determine the angle α between the CN transition moment and the chain axis, at 2238 cm^{-1}, of SAN copolymers containing from 9 to 38 % AN units. This angle was found to be 90°.

Introduction

One of the requirements for studying the orientation of polymer blends by infrared dichroism is that each component exhibits characteristic absorption bands, which do not overlap with others in the infrared spectrum. This is generally possible for polymers containing cyano (CN) groups because it exhibits an infrared absorption band at a wavenumber of about 2238 cm^{-1} where few vibration modes are infrared active. The determination of the orientation function by the infrared dichroism measurements also requires the knowledge of the angle between the transition moment vector of the vibration under consideration and the chain axis, hereafter called the transition moment angle α. However, the α value of the CN vibration in polymers remains uncertain. A value of 61.7° was used by Wang and Cooper for poly(butadiene-co-acrylonitrile) (1) and 90° by Read and Stein for poly(ethylene-co-acrylonitrile) (2), but these two values are different from that of 70.1° (average value for poly(acrylonitrile)) reported in Ref. 3 cited by these two groups. Therefore, it is necessary to reassess this angle such that polymers containing acrylonitrile segments can be readily used to study their orientation in polymer blends. The purpose of this paper is to do so using a series of poly(styrene-co-acrylonitriles) (SAN).

Infrared dichroism allows the determination of the average orientation over all segments with respect to the stretching direction through the measurements of the parameter P_2 which is defined as

$$P_2 = (3\langle\cos^2\theta\rangle - 1)/2 \qquad (1)$$

where θ is the angle between the chain axis and the stretching direction. This parameter is defined by the relation

$$P_2 = (R_0+2)/(R_0-1) \cdot (R-1)/(R+2) \qquad (2)$$

in which the dichroic ratio $R = A_\parallel/A_\perp$, where $A_\parallel$ and $A_\perp$ are the absorbances with the electric vector parallel and perpendicular, respectively, to the stretching direction, and

$R_0 = 2 \cot^2\alpha$ where α is the transition moment angle, as defined before.

Under uniaxial stretching conditions, it can be seen from Eq. 2 that if the angle α is between 0 and 54.7°, then R must be larger than unity (parallel infrared dichroism) in order to keep P_2 positive. If the angle α is between 54.7 and 90°, then R must be smaller than unity (perpendicular infrared dichroism).

In SAN copolymers, the determination of P_2 of styrene segments can be done through infrared dichroism measurements using the absorption band at 1028 cm^{-1}, which does not overlap with any absorption band of the acrylonitrile groups. This band is assigned to the ν_{18a} in-plane CH bending mode of the aromatic ring and its transition moment is perpendicular to the chain axis (4), i.e., $\alpha = 90°$ and $\cot^2\alpha = 0$. Similarly, P_2 can be measured from the 2238 cm^{-1} band corresponding to the ν_{CN} stretching mode, which gives the chain orientation averaged over all AN segments.

It was proposed that the average orientation of A and B segments of an AB random copolymer is necessarily the same (5). Making this assumption, $P_{2(1028)} = P_{2(2238)}$, and the transition moment angle α of the CN vibration at 2238 cm^{-1} in SAN copolymers can be readily determined from the slope of $P_{2(1028)}$ versus $(R-1)/(R+2)_{(2238)}$ (Eq. 2).

Experimental

In this study, six random SAN copolymers containing from 9 to 38 wt % AN units were used. The main characteristics of these polymers are given in Table 1. SAN25 and SAN30 were purchased from Aldrich Chemicals, the other four SAN copolymers were provided by Asahi Chemicals (Japan). Thin films of about 40 µm in thickness were prepared by casting from 5 % methyl ethyl ketone solutions onto glass plates. They were dried under vacuum at 65 °C for 3 days and, then, at 120 °C for 2 days in order to remove residual solvent and internal stress. The chain orientation was induced by stretching the films (20 mm in length and 6 mm in width) with an apparatus, constructed in the laboratory, that allows linear deformation at a constant strain rate and a controlled temperature (± 0.5 °C). Following stretching, the samples were quenched to room temperature in order to freeze in the chain orientation. Polarized infrared measurements were performed with a Mattson Sirius 100 Fourier transform infrared (FTIR) spectrometer, at a resolution of 4 cm^{-1}, making 100 scans for each spectrum. The infrared beam was polarized by a wire-grid polarizer, the sample being rotated 90° for the two absorbance measurements.

Results and discussion

Figure 1 shows the plot of $P_{2(1028)}$ versus $-(R-1)/(R+2)_{(2238)}$ (a negative sign is added because $R_{(2238)} \leq 1$, the CN group exhibiting perpendicular infrared dichroism) for the six SAN samples. As this plot does not depend upon the stretching conditions (4), Fig. A.1 includes data obtained from samples stretched at different draw ratios λ ($\lambda = l_0/l$, where l_0 and l are the sample length before and after stretching, respectively) and at several temperatures above Tg, as indicated in Table 1, with a constant strain rate of 0.115 s^{-1}. The figure also gives the lines corresponding to the transition moment angle α as 61.7, 70.1 and 90°. It is found, despite some scatter in the data points, that most of experimental points are located close to the line which corresponds to $\alpha = 90°$.

Table 1 : Polymers used

Acronym	AN wt %	M_w * 10^{-3}	M_w/M_n	Tg (°C)	T (°C)*
SAN9.5	9.5	289	1.96	106	116
SAN19.5	19.8	248	2.03	109	119
SAN25	23.4	258	1.81	110	120
SAN30	28.3	313	1.89	111	121,126 131,136
SAN34	31.8	252	1.84	112	122
SAN40	38.2	177	1.87	114	124

*stretching temperature.

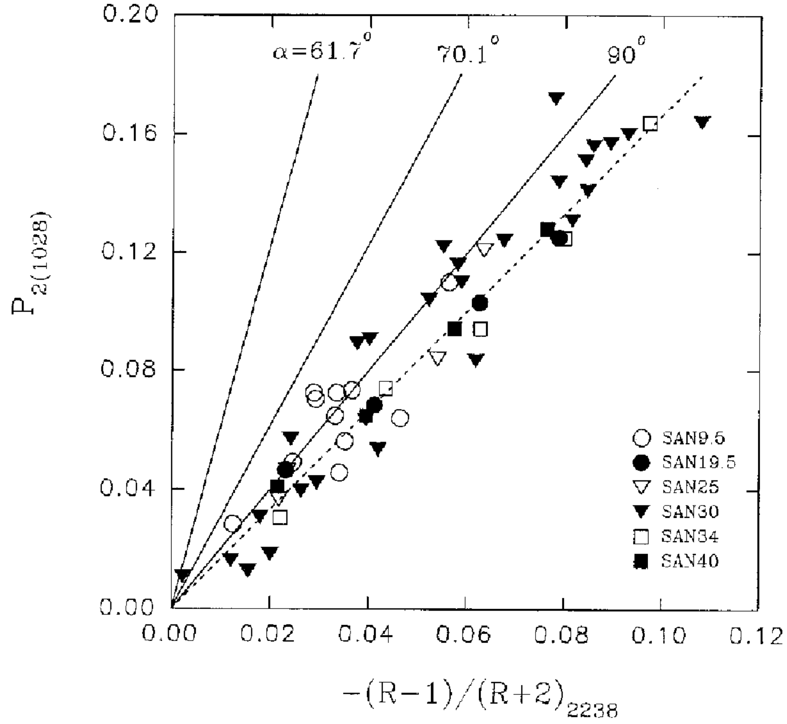

Figure 1. $P_{2(1028)}$ as a function of $-(R-1)/(R+2)_{2238}$ for six random SAN copolymers containing from 9 to 38 wt % AN units. The different lines correspond to CN transition moment angles α of 61.7, 70.1 and 90°, as indicated.

It can also be seen in Fig. 1 that, except for SAN9.5, all SAN copolymers follow the dashed line indicated on the right-hand side of the figure better than the α = 90° line. Since the CN transition moment angle in SAN copolymers cannot be larger than 90° due to its perpendicular infrared dichroism, there is a slight disagreement between theory and experiment, meaning that the assumption that $P_{2(1028)} = P_{2(2238)}$ for SAN copolymers containing a certain level of AN units (> 9.5 wt %) is questionable. In other words, it seems that the orientation of the S segments ($P_{2(1028)}$) in the SAN copolymer is smaller than that of the AN segments ($P_{2(2238)}$).

Several reasons can be considered for such a disagreement between $P_{2(1028)}$ and $P_{2(2238)}$ in SAN copolymers. For example, it was found that, for pure poly(vinyl chloride), the segments having syndiotactic, isotactic and *gauche* conformations each exhibit a different orientation due to different rigidities (6,7). Therefore, it may be considered that different values of $P_{2(1028)}$ and $P_{2(2238)}$ in SAN copolymers can be due to some changes in conformation related to the appearance of triads made of AN units when SAN contains 25 or more mol % AN units (>14.5 wt. %) (8,9). Indeed, the presence of dipole-dipole interactions in consecutive AN units may restrict segmental mobility, thereby leading to a different rigidity of those triads as compared to other segments. Another possible explanation is that the relaxation rate may be different for the two kinds of segments in the SAN copolymers. It has been shown using solid-state NMR spectroscopy that, in poly(α methylstyrene-b-styrene) in the homogeneous state (a single Tg), the A and B segments exhibit different chain dynamics with changes of the block composition (10). However, there is no report on the chain dynamics of a random AB copolymer, and this hypothesis needs to be verified by solid-state NMR spectroscopy.

Conclusions

In summary, the angle α between the CN transition moment and the chain axis at 2238 cm^{-1} is found to be 90°, using infrared dichroism measurements and SAN copolymers containing from 9 to 38 % AN units, in agreement with the value of Read and Stein (2). It is also demonstrated, for the same copolymers, that the orientation function averaged over all AN segments is slightly larger than that averaged over all S segments.

This conclusion agrees with a recent thesis (11) where measurements of the angle α between the CN transition moment and chain axis were also made for a SAN copolymer containing 27 wt % AN; α was found to be 90°. However, the disagreement noted above about the assumption $P_{2(1028)} = P_{2(2238)}$ was not observed in ref. 11, probably because only one composition of the SAN copolymer was used. Nevertheless, this difference can be seen in several copolymers, including a series of random poly(styrene-co-methyl methacrylate), where S and MMA segments exhibit different orientations, as reported in the same study (11).

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