Infrared Absorption Spectra of Alternating Copolymers of Butadiene with Acrylonitrile and Deuterated Analogues

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ABSTRACT: Polarized IR spectra of alternating copolymers and random ones of butadiene with acrylonitrile have been investigated in the region from 4000 to 250 cm^{-1} . The spectra of deuterated alternating copolymers have also been measured. It has been found that dichroism appears to a marked extent when films of the alternating copolymer are elongated, whereas it is hardly observable for the random one. The results were discussed from a viewpoint of orientation of polymer molecules and crystallites in the films of alternating copolymer. Tentative assignments of the absorption bands were made with reference to the results for *trans*-1,4-polybutadiene and those for polyacrylonitrile. The molecular structure of the alternating copolymer is discussed.

KEY WORDS Butadiene / Acrylonitrile / Alternating Copolymer / Deuterated Copolymer / Polarized IR Spectrum / IR Dichroism / X-ray Diagram / Assignment of IR Spectrum / Conformation of Copolymer

Random copolymers consisting of various amounts of butadiene and acrylonitrile have been prepared by conventional radical initiators or Ziegler—Natta catalysts. Recently, a novel alternating copolymer of butadiene with acrylonitrile was successfully prepared by the authors using a system of organoaluminum halide—transition metal compound as a catalyst.^{1,2} The NMR and X-ray analyses of the alternating copolymer indicated a high alternating regularity and *trans* regularity of the butadiene unit.^{2,3} Studies of mechanical properties of the copolymer suggested³ that the alternating copolymer was more flexible and stronger than the random copolymers.

This report deals with a study of the IR spectra under stretching of the alternating copolymer influenced by the regularity of the molecular structure. The IR spectra of *trans*-1,4-polybutadiene have been studied by several

authors^{4–7} and the assignments of the absorption bands of polyacrylonitrile have been given by Liang⁸ and Tadokoro, *et al.*^{9,10} Tentative assignments of the absorption bands of the alternating copolymer were attempted on the basis of IR spectra and IR dichroism of partially deuterated copolymers and correlations with the results obtained on the above mentioned homopolymers.^{4,6,7,9,10}

EXPERIMENTAL

The copolymerization procedures are almost the same as those in the preceding paper.¹ The alternating copolymerization of butadiene with acrylonitrile was carried out at 0°C for 24 hr with EtAlCl_2 as a complexing agent and VOCl_3 as a cocatalyst. The random copolymer was prepared at 50°C by the use of benzoyl peroxide (BPO) as an initiator. Table I summarizes the polymerization conditions and results.

A sample of 1, 1, 4, 4-tetradeuterobutadiene

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Table I. Polymerization conditions and results^a

	Alternating copolymer		Random copolymer
	A-4	A-4'	
$[\eta]_{\text{DMF}}^{30^\circ\text{C}}$, dl/g	2.06	2.50	3.17
AN content, mol %	48.5	48.8	48.3
Fraction of alternating dyad, mol %	94	93	84

^a Alternating copolymerization: AN/BD, 1/1 (mol/mol); $\text{EtAlCl}_2/\text{VOCl}_3$, 50/1 (mol/mol); $\text{Al}/(\text{AN} + \text{BD})$, 5/100 (mol/mol); 0°C ; 24 hr. Random copolymerization: AN/BD, 7/3 (mol/mol); BPO, 3 mol %; 50°C ; 5 hr.

(butadiene- d_4) was prepared^{11,12} by thermal decomposition of 2, 2, 5, 5-tetra-deuterobutadiene- β -sulfone which was obtained by the isotope exchange reaction of butadiene- β -sulfone (supplied from Seitetsu Kagaku Co., Ltd.) in the presence of deuterium oxide and a small amount of potassium carbonate. The isotopic purity of butadiene- d_4 was estimated to be *ca.* 95% from its NMR spectrum. A sample of α -deuteroacrylonitrile (acrylonitrile- d) was prepared^{13,14} by the isotope exchange reaction of acrylonitrile in the presence of deuterium oxide and a small amount of calcium oxide. Its isotopic purity was *ca.* 96%.

IR analysis of the alternating copolymer was made by a Perkin-Elmer model 521 grating spectrophotometer using thin films. Polarized spectra were recorded on the same instrument when equipped with a wire grid polarizer. Differential polarized spectra¹⁵ of the copolymer were obtained with a Hitachi model EPI-S2 spectrophotometer equipped with two silver chloride polarizers. The IR measurements at low temperatures were carried out by the use of Wager and Hornig-type apparatus.¹⁶ X-Ray diffraction diagrams were obtained by a Shimadzu GX-2 X-ray diffractometer.

RESULTS

The IR spectra of the alternating copolymer of butadiene with acrylonitrile indicate that the diene unit in the polymer is of a *trans*-1,4-configuration, and the absorption bands assignable to the vinyl or *cis*-1,4-configuration are

almost or completely absent. The spectra of the alternating copolymer were almost the same as those of the random one.¹ However, the difference between the alternating copolymer and the random one are obvious in the polarized IR spectra.

Figure 1 shows the differential polarized IR spectra of the copolymer films stretched by 1100%. Bands perpendicular (σ) and parallel (π) to the stretching direction show the downward and upward peaks, respectively. In the alternating copolymer strong perpendicular peaks appear at 2930, 2240, 1455, and 970 cm^{-1} and parallel peaks at 1665, 1305 and 1075 cm^{-1} . The IR dichroism is observed much more clearly in the alternating copolymer than in the random one. This suggests that there exist stronger specific intra- or inter-molecular interactions in the alternating copolymer allowing molecular orientation under stretching. In general, the crystallization occurs in the copolymers having a long alternating sequence. It was known that the average length of the alternating sequence increases rapidly at a high regularity of dyad sequence.* Therefore, the crystallinity may be significant only for the copolymer of high alternating dyad. Indeed, the enhanced tensile properties caused by crystallization on stretching are observed for the alternating copolymer of high dyad-sequence regularity.¹⁷ The X-ray diffraction diagrams of the stretched polymer films indicate the pattern of crystallization-imposed orientation in the alternating copolymer in contrast to

* The average length (l_{1221}) of alternating sequence is given by the following equation (K. Tada, T. Fueno, and J. Furukawa, *J. Polym. Sci., Part A-1*, **4**, 2981 (1966)) with alternating dyad fraction F_{12} and F_{21} and fraction of monomer unit F_1 and F_2 .

$$l_{1221} = \frac{2}{F_{11}/F_1 + F_{22}/F_2}$$

At $F_1 = F_2 = 0.5$, it follows that

$$l_{1221} = \frac{1}{1 - (F_{12} + F_{21})}$$

For example, l_{1221} is 6 and 14 for the copolymers whose $F_{12} + F_{21}$ is 0.84 and 0.93, respectively. In other words, l_{1221} increases very rapidly when the value of the alternating dyad is close to unity.

Figure 1. Differential polarized IR spectra of copolymers stretched by 1100% at 20°C.

Figure 2. X-Ray diffraction diagram of copolymer films stretched by 700% at room temperature.

an amorphous halo in the random one as shown in Figure 2.

The IR dichroism of the alternating copolymer and the random one was investigated at 1100-% elongation in order to elucidate the detailed differences between the spectra of both copolymers. The results are shown in Figure 3. The solid and broken lines represent the absorption curves for the polarized radiations

with the electrical vectors perpendicular (σ) and parallel (π) to the stretching direction, respectively. The dichroic ratios thus calculated are shown in Table II. As will be described later, the dichroic ratios give information about the molecular structure of the alternating copolymer.

Figure 4 shows the polarized IR absorption spectra of the stretched films at 20° and -180°C. The bands indicated by the arrows are sensitive

Infrared Absorption Spectra of Alternating Copolymers

Figure 3. Polarized IR spectra of copolymers stretched by 1100% at 20°C: ---, π ; —, σ .

Table II. Infrared dichroism of alternating and random copolymers; from Figure 3

Frequency, cm^{-1}	Intensity ^a	D_{π}/D_{σ}		Dichroism
		Alternating copolymer	Random copolymer	
2990	sh	0.68	1.00	σ
2930	vs	0.63	1.00	σ
2850	s	0.62	1.00	σ
2240	vs	0.45	0.90	σ
1665	w	1.64	1.50	π
1455	vs	0.48	0.91	σ
1440	vs	0.57	0.97	σ
1365	sh	0.76	1.00	σ
1345	m	0.78	1.04	σ
1305	m	1.38	1.17	π
1075	m	1.49	1.15	π
970	vs	0.58	0.93	σ
475	w	2.04	—	π

^a vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table III. Effect of measurement temperature on dichroic ratio; from Figure 4

Frequency, cm^{-1}	D_{π}/D_{σ} of alternating copolymer		Dichroism
	at 20°C	at -180°C	
1286	1.29	1.30	π
1210	0.98	0.72	σ
1075	1.57	1.64	π
840	—	0.44	σ
835	0.76	—	σ
735	0.91	0.89	σ
555	0.76	0.67	σ
530	0.91	0.63	σ
475	2.16	2.74	π

to temperature and become strong at -180°C . The dichroic ratios for these bands calculated from Figure 4 are listed in Table III. These peaks may be ascribed to bands sensitive to crystallization.

As further evidence, the IR spectra of partially deuterated polymers are shown in Figure 5. The spectra offer information useful for the assignment of bands. The frequency, relative intensity and polarization are listed in Table IV. The assignments described in the last column of Table IV will be discussed in the following section.

Figure 4. Polarized IR spectra of alternating copolymer (A-4') stretched by 600%: ---, π ; —, σ . The absorptions at 3600–3500, 3200, and 1720 cm^{-1} are due to $-\text{CONH}_2$ and H_2O impurity.

Figure 5. IR spectra of alternating copolymer of BD-AN (a), BD- d_4 -AN (b), and BD- d_4 -AN- d (c) at 20°C.

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Table IV. Observed frequencies (in cm^{-1}) and assignments for the alternating copolymers; from Figure 5

	BD-AN	BD- d_4 -AN	BD- d_4 -AN- d	Assignment ^a
σ	3030 m, sh ^b	3020 s	3020 s	BD ν CH
σ	2985 m, sh			BD (2980, combination)
σ	2950 s, sh			BD ν_a CH ₂
σ	2925 vs, b	2925 vs	2925 vs	AN ν_a CH ₂ + [AN ν CH]
σ	2852 s, b	2860 s	2860 s	AN ν_s CH ₂ + [BD ν_s CH ₂]
σ	2235 vs	2240 vs	2240 vs	AN ν CN
σ		2202 s	2200 s	BD ν_a CD ₂
σ		2108 s	2106 s	BD ν_s CD ₂
π	1665 w	1662 w	1662 w	BD ν C=C
σ	1448 vs, sh	1448 s	1448 s	AN δ CH ₂ + [BD δ CH ₂]
σ	1440 vs			BD δ CH ₂
σ	1365 m, sh	1350 m, sh		AN δ CH
σ	1345 m, b	1328 m	1328 m	AN ω CH ₂ + [BD ω CH ₂]
π	1295 m, b	1290 m	1290 m	BD ω CH+ ν C-C
π	1268 w, sh	1262 m	1265 m, b	BD ω CH+ ν C-C
	—	1235 w, sh		AN ω CH
σ	1210 w, b			BD ω CH ₂
σ			1170 m, b	—
σ	1100 w, sh	1125 w, sh	1125 w, sh	ANtCH ₂
σ		1080 m, sh	1080 m	BD δ CD ₂
π	1075 m	1072 m	1065 sh	AN ν C-C+ [BD δ CD ₂]
π	1050 m, b	1035 m	1038 sh	BD ν C-C
		1010 m, sh	1010 m, sh	BD ω CD ₂
σ	970 vs	968 vs	970 vs	BD δ CH
	925 m, sh	935 m	930 m	ν C-C
σ		890 w, sh	890 w, sh	BD ω CD ₂
σ	820 w, b	820 w, b	810 w, b	AN γ CH ₂
σ	745 w, b	738 m	742 m	AN ν C-CN+ [BD γ CH ₂]
σ		658 w, b	660 w	—
		605 w	600 w	BD γ CD ₂
σ	540 w, b	520 m	510 w	AN δ C-CN
π	440 b	430 w, b	430 w, b	AN δ CN+ BD (440)

^a AN, of acrylonitrile unit; BD, of butadiene unit; ν , stretching; ν_a , antisymmetric stretching; ν_s , symmetric stretching; δ , bending; ω , wagging; t, twisting; γ , rocking. Assignments in [] are to be applied to some of the isotopic species. BD (2980) implies that the corresponding band appears at 2980 cm^{-1} in *trans*-polybutadiene.

^b See Table II. b, broad.

DISCUSSION

As reported in a previous paper,¹ no differences between the IR spectra of the alternating copolymer and the random one were seen although NMR spectra of the alternating copolymer and the random one are distinguishable from each other by the difference in the degree of alternation.¹ In the IR dichroism both polymers differ clearly. Random copolymers are very difficult to crystallize and provide no appreciable IR di-

chroism. The dichroic behaviour in the alternating copolymer was found to be associated with sequential regularity. The identical period, $7.16\text{ \AA}$ is calculated from the X-ray diffraction patterns. This seems to differ from the identical period of a planar-zigzag chain structure (of $7.5\text{ \AA}$). The space group of the copolymer is not established at present.

Analysis of IR Spectrum

The alternating copolymer possesses two kinds

of CH_2 due to the butadiene and acrylonitrile units. Most of the CH_2 stretching modes can be readily analyzed on the basis of previous studies of other polymers. The perpendicular bands at 2985, 2950, 2925, and 2852 cm^{-1} can probably be assigned to the modes shown in Table IV. These assignments are compatible with the difference in the intensity between the deuterated and nondeuterated copolymers. The corresponding modes for polyacrylonitrile and *trans*-1,4-polybutadiene are observed at almost the same positions. The perpendicular band at 3030 cm^{-1} is assigned to the CH stretching mode of the butadiene unit, whereas the CH stretching mode for the acrylonitrile unit is not so clear, and probably is involved in the band at 2925 cm^{-1} . The CN stretching mode (σ) and the C=C stretching mode (π) can be easily found to be at 2235 and 1665 cm^{-1} , respectively. The CH_2 bending modes appear as a doublet at 1448 and 1440 cm^{-1} . The latter is assigned to the band due to the butadiene units, because the band disappeared in the copolymer prepared from butadiene- d_4 .

The assignment of the bands at the wave number lower than 1400 cm^{-1} is more difficult, because various types of CH deformation and skeletal modes appear in this region coupled with each other. The band at 1365 cm^{-1} probably contains the CH bending mode of the acrylonitrile unit. This assumption is rationalized by comparing Figure 5b with Figure 5c. The band at 1345 cm^{-1} is assigned to the " CH_2 wagging" mode of the butadiene bonded to the α -carbon of acrylonitrile and the acrylonitrile unit, since the intensity is decreased in the polymer from butadiene- d_4 . The parallel bands at 1295 and 1268 cm^{-1} are assigned to the "CH wagging" mode of the butadiene unit coupled with the C—C stretching mode, which are still remain in the copolymer of butadiene- d_4 with acrylonitrile- d . The " CH_2 wagging" mode of butadiene unit bonded to β -carbon of acrylonitrile is most likely to be the origin of the 1210 cm^{-1} band, which disappeared in the polymer from butadiene- d_4 , because the band at 1210 cm^{-1} may correspond to the band at 1235 cm^{-1} for *trans*-1,4-polybutadiene assigned to the " CH_2 wagging" by Neto, *et al.*⁷ The parallel bands at 1075 and 1050 cm^{-1} may contain

the contributions from the C—C stretching mode of the acrylonitrile and the butadiene unit, respectively. The corresponding modes for polyacrylonitrile and *trans*-1,4-polybutadiene are observed at almost the same position together with the combination of the fundamentals. The band at 970 cm^{-1} is assigned to the "CH bending" mode of the butadiene unit. The corresponding mode for *trans*-1,4-polybutadiene is observed at 967 cm^{-1} . The band at 925 cm^{-1} may contain the contribution from the C—C stretching mode. The perpendicular bands at 820 and 745 cm^{-1} may correspond to the bands at 865 and 778 cm^{-1} in polyacrylonitrile which are assigned to the " CH_2 rocking" and "C—CN stretching" modes, respectively.

The crystallite-sensitive bands for *trans*-1,4-polybutadiene have been observed at 1235, 1051, 772, and 445 cm^{-1} by Nikitin, *et al.*,⁴ at 1250, 1053, 972, and 775 cm^{-1} by Binder,⁵ 1054 and 440 cm^{-1} by Neto, *et al.*,⁷ or at 1242, 1055, and 772 cm^{-1} by Furukawa, *et al.*¹⁸ In the alternating copolymer of butadiene with acrylonitrile, the crystallite-sensitive bands seem to appear at the wavenumbers listed in Table III. Some bands are shifted from the position shown in Figure 5a. This shift may be due to the change in an intermolecular force field caused by crystallization.

Estimation of Molecular Structure

The degree of molecular orientation of the alternating copolymer of butadiene with acrylonitrile is expressed as a function of IR dichroic ratio ($D=A_\pi/A_\theta$) by eq 1.¹⁹

$$\frac{D-1}{D+2} = f \times \frac{3 \cos^2 \theta - 1}{2} \quad (1)$$

Here A_π and A_θ are the absorbances for parallel and perpendicular radiations, respectively, f is the average degree of orientation of the polymer chain, and θ is the angle between the axis of the polymer chain and the transition moment of the absorption band. The f -value can be calculated from the value of A_π/A_θ at 2240 cm^{-1} , by assuming that the angle between the transition moment of the CN stretching mode and the axis of polymer chain is 90°. Then the average angle θ_A which is defined as $\cos^2 \theta_A = \overline{\cos^2 \theta}$, can be obtained for some of the bands.

From the data of Table II, the values of θ_A for the 1665 cm^{-1} ($\nu_{\text{C}=\text{C}}$) and 1455 cm^{-1} ($\text{AN } \delta_{\text{CH}_2}$) bands are estimated to be about 39° and 82° , respectively. The θ_A value seems to increase with the stretching ratio. These values may be regarded as a measure of the relative arrangement of the groups. Assuming the $\text{C}=\text{C}$ $1.34\text{ \AA}$, $\text{C}-\text{C}$ $1.5\text{ \AA}$, $\text{C}-\text{C}-\text{C}$ 109° , and $\text{C}=\text{C}-\text{C}$ 120° ,⁴ the molecular structure is expressed as in the following formula. The angle between $\text{C}-\text{CN}$, $\text{C}-\text{H}_2$ or $\text{C}=\text{C}$ and the chain axis is calculated to be 90° , 90° or 24.5° , respectively.

The discrepancy between the value of the angles or identical periods estimated from the molecular model and eq 1 or X-ray diagram may suggest a nonplanar-zigzag conformation and a somewhat twisted chain conformation. In the case of *trans*-1,4-polybutadiene, it was also indicated⁴ by infrared dichroic measurements that the molecular chains do not have a flat *trans*-conformation but are somewhat folded.

A theoretical study of the spectra of the alternating copolymer of butadiene with acrylonitrile would be interesting to assess the correctness of some of the assignments mentioned above.

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