Infrared Spectra of Alternating Copolymer of Butadiene and Methyl Methacrylate

Junji FURUKAWA, Eiichi KOBAYASHI,* and Yoshihiro ARAI*

*Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto 606, Japan.*

(Received February 4, 1974)

ABSTRACT: The infrared spectra of butadiene-methyl methacrylate alternating and random copolymers were investigated. It was found that the polarized infrared spectra of the elongated films of alternating copolymers showed a remarkable dichroism, whereas for the random copolymers, with poor stretching properties, dichroism could not be observed. The tentative assignments of the infrared spectra of the alternating copolymer were made with reference to the results for each homopolymer and the partially deuterated alternating copolymer prepared from 1, 1, 4, 4-tetradeuterobutadiene and methyl methacrylate.

The X-ray diffraction diagram from an elongated film of the alternating copolymer showed a pattern of crystallization-imposed orientation. The characteristics of sequential regularity indicated by the X-ray data for the copolymer have been confirmed already with NMR data.

Similarities such as the identical 7.17 Å period were recognized between the alternating copolymers of butadiene-acrylonitrile and butadiene-methyl methacrylate.

KEY WORDS Butadiene / Methyl Methacrylate / Alternating Copolymer / Polarized IR Spectrum / IR Dichroism / X-Ray Diagram / Assignment of IR Spectra / Identical Period of Alternating Copolymer /

The infrared spectrum of the alternating copolymer of butadiene and acrylonitrile was almost identical to that of the random copolymer.¹ However, appreciable differences were observed in the polarized infrared spectra measured with stretched samples of each copolymer.² The sequential regularity of the alternating copolymer favors orientation and crystallization under stretching so that it shows a pronounced infrared dichroism. This sequential regularity for the alternating copolymers of butadiene with acrylonitrile and butadiene with methyl methacrylate has already been confirmed by 100- and 220-MHz NMR spectra.³

In the present work, the infrared spectrum and X-ray diffraction diagram of the alternating copolymer of butadiene and methyl methacrylate were studied. The tentative assignment of the infrared spectra of the copolymer was also investigated by using deuterobutadiene.

* Present address: *Institute for Chemical Research, Kyoto University, Uji 611, Japan.*

EXPERIMENTAL

1, 1, 4, 4-Tetradeuterobutadiene (BD-*d*₄) was prepared according to the method of Ikeda, *et al.*⁴ The detailed procedures were described previously.²

The purification of the reagents and the polymerization procedures are almost the same as those in a previous report.⁵ The polymerization conditions and results are summarized in Table I.

The copolymer films were prepared by casting methylene chloride solutions of the copolymers on mercury metal followed by evaporating the solvent under reduced pressure. The films thus obtained were stretched to an elongation of about 8 times at 70–80°C and then clamped so as to retain their length. The films of random copolymer could be not elongated without rupture.

The infrared spectra of the copolymer films were measured with a Perkin-Elmer model 521

Table I. Polymerization conditions and results of BD—MMA copolymer in bulk

Monomer	Catalyst	Temp, °C	Time, hr	Conv, %	[MMA] in copolymer ^c , %	$[\eta]^d$, dl/g
BD—MMA	EtAlCl ₂ —VOCl ₃ ^a	0	20	12.5	52.0	4.1
BD- <i>d</i> ₄ —MMA	EtAlCl ₂ —VOCl ₃	0	4	63	51.7	1.8
BD—MMA	Benzoyl peroxide ^b	50	3	3.1	62.9	—
BD- <i>d</i> ₄ —MMA	Benzoyl peroxide	50	7.5	4.9	55.4	0.5

^a [EtAlCl₂]/[Total monomer], 1/25; [VOCl₃]/[EtAlCl₂], 1/100.^b [Benzoyl peroxide]/[Total monomer], 1/50.^c The copolymer composition was calculated from the elemental analysis of oxygen.^d $[\eta]$ was determined in toluene at 30°C. **Figure 1.** Infrared spectra of alternating BD—MMA, BD-*d*₄—MMA copolymer, and random BD—MMA, BD-*d*₄—MMA copolymer.

grating spectrophotometer. Polarized spectra were recorded on the same instrument equipped with a wire grid polarizer. Differential polarized spectra⁶ of the copolymer films were obtained with a Hitachi model EPI-S2 infrared spectrophotometer equipped with two silver chloride polarizers. These were measured at room temperature. The X-ray diffraction diagram was obtained with Shimadzu GX-2 X-ray diffractometer at room temperature.

RESULTS

The infrared spectra of the unstretched film of the alternating copolymer of butadiene and methyl methacrylate and the random copolymer together with their deuterated analogues are shown in Figure 1. Some of the spectral absorptions are similar to those of the alternating copolymers of butadiene and acrylonitrile. Namely, the diene unit in the alternating copolymers is in the *trans*-1,4-configuration (970 cm^{-1}), with the vinyl (993 cm^{-1}) and/or *cis*-1,4-configuration (740 cm^{-1}) almost or completely unobserved. The spectra of the alternating copolymers of butadiene and methyl methacrylate are almost identical to those of

the random one. However, the bands in the region from 1300 to 1200 cm^{-1} , which corresponds to the tacticity-sensitive area for poly-(methyl methacrylate),⁷ are somewhat different from each other.

The polarized infrared spectra of the alternating copolymer films stretched by 700% are shown in Figure 2. The solid and broken lines represent the absorption curves obtained for the polarized radiation with the electric vectors perpendicular (σ) and parallel (π) to the stretching direction, respectively. The infrared dichroism is evident in the alternating copolymer of butadiene and methyl methacrylate just as it is in the copolymer of butadiene and acrylonitrile.² However, the infrared dichroism of the random copolymer of butadiene and methyl methacrylate could not be measured. The differential polarized infrared spectra of the alternating copolymer films stretched by 700% are shown in Figure 3. The bands perpendicular (σ) and parallel (π) to the stretching direction are shown by downward and upward peaks, respectively. Strong perpendicular peaks appear at 2910 , 1740 , 1710 , 1465 , 1380 , 1330 , 1220 , and 965 cm^{-1} and parallel peaks at 2970 , 1665 and 920 cm^{-1} . The polarized and the differential polarized infrared

Figure 2. Polarized spectra of alternating BD—MMA and BD- d_4 —MMA copolymer film elongated by 700%: (—), electric vector perpendicular to direction of stretch; (---), electric vector parallel to direction of stretch.

Figure 3. Differential polarized spectra of alternating BD-MMA and BD-d₄-MMA copolymer film elongated by 700%.

spectra of the alternating copolymer suggest that the sequentially regular copolymer favors generating molecular orientation under stretching.

Figure 4. X-Ray diffraction diagram of alternating copolymer of BD-MMA elongated by 700%.

In fact, the X-ray diffraction diagram of the stretched copolymer film indicates a pattern of crystallization-imposed orientation as shown in Figure 4. A repetitive interval of 7.17 Å is calculated from the X-ray diffraction pattern. This seems to differ from the repetitive interval of a planar-zigzag chain structure of 7.5 Å² estimated from a molecular model, and suggests a somewhat twisted chain conformation as mentioned in a previous paper.^{2,3}

DISCUSSION

The frequency, relative intensity, polarization, and tentative assignment of the alternating copolymer and deuterated analogues are listed in Table II. The assignment was attempted by referring to that of poly(methyl methacrylate)⁷ and that of *trans*-1,4-polybutadiene.^{8,9}

The band at 3430 cm⁻¹ is easily assigned to the overtone of the C=O stretching vibration at 1728 cm⁻¹. The alternating copolymer of

Infrared Spectra of BD—MMA Alternating Copolymer

Table II. Infrared spectra of alternating BD—MMA and BD-*d*₄—MMA copolymer (from Figure 1)

BD—MMA			BD- <i>d</i> ₄ —MMA			Tentative assignment ^b
Frequency, cm ⁻¹	Relative intensity ^a	Polarization	Frequency, cm ⁻¹	Relative intensity ^a	Polarization	
3430	vw, b	σ	3430	vw, b	σ	2ν(C=O)[MMA]
3020	m, sh	σ	3010	sh	σ	ν(CH)[BD]
2970	m, sh	π	2978	m	π	ν _a (CH ₃ —O)[MMA] + ν _a (CH ₂)[MMA]
2940	s	σ	2940	m, sh	σ	ν _a (CH ₂)[BD] + {ν _s (CH ₃ —O) + ν _a (α-CH ₃) + ν _s (α-CH ₃) + ν _s (CH ₂)}[MMA]
			2928	s	σ	
2920	sh	σ	2915	sh	σ	Combination band associated with ester CH ₃ group [MMA]
2875	sh	σ	2873	sh	σ	
2845	m	σ	2848	m	σ	ν _s (CH ₂)[BD] + } Combination band [MMA]
			2193	m	σ	ν _a (CD ₂)[BD]
			2100	m, b	σ	ν _s (CD ₂)[BD]
1736	vs, sh	σ	1738	vs	σ	} ν(C=O)[MMA]
1728	vs	σ	1730	vs	σ	
1665	w	π	1660	w	π	ν(C=C)[BD]
1473	sh	σ	1473	sh	σ	δ _a (α-CH ₃)[MMA]
1460	s	σ	1458	s	σ	δ _a (CH ₃ —O)[MMA]
1448	s, sh	σ				δ(CH ₂)[BD]
1430	s	σ	1430	s	σ	{δ(CH ₂) + δ _s (CH ₃ —O)}[MMA]
1380	s	σ	1377	s	σ	δ _s (O—CH ₃)[MMA]
1345	sh, b	σ				ω(CH ₂)[BD] +
			1320	sh	σ	ω(CH)[BD] + ω(CH ₂)[MMA] + {ν _a (C—C—O) + ν(C—O)}[MMA]
			1300	s	σ	
			1290	sh	σ	
1295	sh, b	σ	1245	sh	σ	
1268	sh, b	σ	1216	vs	σ	
1245	sh, b	σ				
1216	sh	σ				
1198	vs, b	σ				t(CH ₂)[BO] + {ν(C—C)[MMA] + Skeletal stretching coupled with internal CH deformation vibration [MMA]}
			1193	m, sh	σ	
1140	vs	σ	1136	vs	σ	
			1090	sh	σ	
1080	vw	π	1065	vw, sh	—	ν(C—C)[BD]
			1050	m	σ	δ(CD ₂)[BD]
			1010	sh	σ	ω(CD ₂)[BD]
993	sh	σ	992	sh	σ	δ(CH)[BD] + {ν _s (C—O—C) + γ(CH ₃ —O)}[MMA]
970	vs	σ	975	vs	σ	
905	w	π	935	sh, b	π	γ(α-CH ₃)[MMA]
			875	w	σ	t(CD ₂)[BD]
805	w, b	—	800	w, b	—	^d
762	vw, b	π	765	vw	π	{ν(C—C) + γ(CH ₂)}[BD and MMA] ^d
			730	vw, b	π	
			580 ^c	vw	π	γ(CD ₂)[BD] + —
480 ^c	w, b	σ	475 ^c	w, b	σ	δ(C—C—O)[MMA] ^d
355 ^c	w, b	σ	360 ^c	m, b	σ	^d

^a s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

^b [MMA], of methyl methacrylate unit; [BD], butadiene unit; ν, stretching; ν_a, asymmetric stretching; ν_s, symmetric stretching; δ bending; ω, wagging; t, twisting; γ, rocking.

^c See Figure 2.

^d They may correspond to crystalline sensitive band.

butadiene and methyl methacrylate possesses various kinds of CH_3 , CH_2 and CH , and consequently, the assignment of these modes is rather difficult, because the band contains contributions from combinations or overlaps of the fundamentals. The perpendicular band at 3020 cm^{-1} is assigned to the CH stretching mode and is retained in the $\text{BD-}d_4$ —MMA copolymer. The bands at 2970, 2940, 2920, 2875, and 2845 cm^{-1} are all associated with the ester methyl group. The former two are assigned mainly to the fundamental vibrations of the asymmetric and symmetric stretching of the ester methyl group, and the latter three the combination bands associated with the ester methyl group as shown in Table II. The modes corresponding to poly(methyl methacrylate) were observed at 2995, 2948, 2920, and 2835 cm^{-1} .⁷ These facts are consistent with the above assignment. The band at 2940 cm^{-1} probably contains the CH_2 asymmetric stretching mode of the butadiene unit. This is reasonable from the fact that the frequencies are intermediate between those of *trans*-1,4-polybutadiene and poly(methyl methacrylate). Furthermore, this band is reduced in intensity but does not disappear completely on deuterating the CH_2 group of the butadiene unit. The band at 2845 cm^{-1} is assigned to the overlapping absorption of the CH_2 symmetric stretching mode of the butadiene unit and the combination associated with the ester methyl group. These assumptions are rationalized by a comparison of the intensities of the non-deuterated polymer with those of the deuterated one prepared from $\text{BD-}d_4$. The reasonable values of 1.34 and 1.35 are found respectively for the CH_2/CD_2 frequency ratios of the asymmetric and symmetric vibrational frequencies.

The $\text{C}=\text{O}$ stretching (σ) and the $\text{C}=\text{C}$ stretching (π) mode are responsible for the doublet at 1736 and 1728 cm^{-1} and the band at 1665 cm^{-1} , respectively. The absorption intensity of the $\text{C}=\text{C}$ stretching mode of the butadiene—methyl methacrylate alternating copolymer is weaker than that of the butadiene—acrylonitrile alternating copolymer.² This may be concerned with the symmetry of the molecular structure with respect to the stereospecificity of the α -carbon in the acrylic monomer unit.

In the spectrum of the alternating copolymer, the CH bending modes of the $\alpha\text{-CH}_3$, O-CH_3 and the two kinds of CH_2 are observed in the region from 1473 to 1380 cm^{-1} . The CH_2 bending mode of the butadiene unit is responsible for the band at 1448 cm^{-1} which disappears on deuteration of the butadiene unit. This mode for the alternating copolymer of butadiene and acrylonitrile appeared at 1440 cm^{-1} .² The band at 1345 cm^{-1} , which disappears on deuteration of the butadiene CH_2 group, is assigned to the CH_2 wagging vibrations of the butadiene unit. The corresponding CD_2 vibration in the $\text{BD-}d_4$ —MMA copolymer is observed at 1010 cm^{-1} . The ratio of the CH_2 vibrational frequency to the CD_2 one is 1.33.

The bands at wavenumbers lower than about 1300 cm^{-1} are rather complicated, because the region contains contributions from combinations and overlappings of the fundamental together with the skeletal modes. The broad band at 1295 cm^{-1} may originate from the two wagging modes of the methyl methacrylate CH_2 group and the butadiene CH group. The two inflections at 1268 and 1245 cm^{-1} seem to correspond to the 1270 and 1240 cm^{-1} doublet of syndiotactic poly(methyl methacrylate), which Nagai has assigned to $\nu_a(\text{C-C-O})$ coupled with $\nu(\text{C-O})$.⁷ However, the corresponding inflection at 1245 cm^{-1} in the deuterobutadiene—methyl methacrylate copolymer resembles the single absorption of isotactic poly(methyl methacrylate) at 1249 cm^{-1} . But these absorption intensities are very weak and they do not offer exact information corresponding to cotacticity of the alternating copolymer. According to the 220-MHz NMR spectrum of deuterobutadiene—methyl methacrylate alternating copolymer an isotactic configuration flanked by butadiene units was suggested. Either way, these inflections may be due to the vibrational modes of methyl methacrylate unit described as $\nu_a(\text{C-C-O})$ in Table II. The assignment of these bands may be a skeletal stretching mode coupled with the internal CH deformation modes, as has been pointed out by Nagai.⁷ In particular, the contribution from the C-C-O asymmetric stretching mode is large as is deduced from the high intensity of these bands.

The parallel band at 1080 cm^{-1} is probably assigned to the C—C stretching mode. The band at 1050 cm^{-1} is reasonably assigned to the CD_2 bending mode. The C—O—C symmetric stretching and the O—CH₃ rocking mode are responsible for the bands at 993 and 970 cm^{-1} . The parallel band at 905 cm^{-1} shifted to 935 cm^{-1} on deuteration of the butadiene unit. This band is easily assigned to the $\alpha\text{-CH}_3$ rocking mode.

The intensity of the bands at 805 and 762 cm^{-1} increased with stretching of the copolymer film. In the spectra of poly(methyl methacrylate), it is pointed out that the bands near 750 cm^{-1} increase in intensity owing to crystallization.⁷ This band may be associated with a crystallization-sensitive band. The parallel band at 762 cm^{-1} for the nondeuterated copolymer and the bands 765 , 730 cm^{-1} for the deuterated one may be associated with the C—C stretching and the CH₂ rocking mode. The assignment of the absorptions at 1090 , 805 and 355 cm^{-1} are uncertain at present.

In conclusion, the molecular structures of butadiene—acrylonitrile or —methyl methacrylate alternating copolymer in the crystalline resion, have nearly identical repetetive intervals of $7.14\text{--}7.17\text{ \AA}$. This may reflect the high sequence regularity and similar crystalline structure of

these alternating copolymers prepared by similar polymerization mechanisms.⁵

Acknowledgment. The authors wish to express his grateful to Dr. J. Umemura (Institute for Chemical Research, Kyoto University) for his kind guidance through the assignment of the infrared spectra.

REFERENCES

1. J. Furukawa, Y. Iseda, K. Haga, and N. Kataoka, *J. Polym. Sci., Part A-1*, **8**, 1147 (1970).
2. J. Furukawa, E. Kobayashi, K. Uratani, Y. Iseda, J. Umemura, and T. Takenaka, *Polymer J.*, **4**, 358 (1973).
3. T. Suzuki, Y. Takegami, J. Furukawa, E. Kobayashi, and Y. Arai, *ibid.*, **4**, 657 (1973).
4. S. Ikeda, Y. Tanaka, and T. Morishima, Annual Meeting, Soc. High Polymer Sci., Nagoya, 1962, p 79.
5. J. Furukawa, E. Kobayashi, Y. Iseda, and Y. Arai, *Polymer J.*, **1**, 442 (1970).
6. R. Gotoh, T. Takenaka, and N. Hayama, *Kolloid-Z. Z. Polym.*, **205**, 18 (1965).
7. H. Nagai, *J. Appl. Polym. Sci.*, **7**, 1697 (1963).
8. V. N. Nikitin and N. V. Mikhailova, *Vysokomol. Soedin., Ser. A*, **9**, 784 (1967).
9. N. Neto and C. Di Lauro, *Eur. Polym. J.*, **3**, 645 (1967).