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Infrared Analysis of Copolymers. II. The Sequence Distribution of Methyl Acrylate Units in Methyl Acrylate–Styrene Copolymers

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In the infrared spectra of copolymers, the characteristic stretching vibrations such as the $C=O$ stretching mode in acrylate copolymers, have generally been considered to be independent of the sequence environment. In fact, in methylacrylate (MA)–styrene(ST) copolymers Kamiyama *et al.* noted that no shift of the peak position of the carbonyl absorption band is observed with changes in the composition, although the half-band width decreases regularly with a decrease in the MA content.[1]

However, we recently found that the $C\equiv N$ stretching mode in acrylonitrile(AN)–styrene(ST) copolymers is sensitive to sequence environment and, hence, useful in determining the sequence distribution in AN–ST copolymers.[2] In order to ascertain whether this is a phenomenon characteristic of all copolymers with polar groups, the infrared spectra of MA–ST copolymers were studied.

Experimental

The random copolymers were prepared by copolymerizing MA and ST monomers, with benzoyl peroxide as the initiator, at 60°C. The low-conversion copolymers thus obtained were used for the infrared measurement. The MA–ST copolymer prepared with ethylalminum sesquichloride[3] was also used. These samples are listed in Table 1. The MA contents of copolymers were determined by NMR spectrometry.

The infrared spectra were recorded in a benzene solution with a Hitachi-Perkin Elmer 125 grating infrared spectro-

Table 1. Sequence distribution in methyl acrylate–styrene copolymers

Mole % of MA		Conversion (%)	νC=O (cm^{-1})	P_{MM} (obsd)	P_{MM} (calcd)	P_{MMM} (calcd)
Feed Mixture	Copolymer					
100	100	—	1739.6	—	1.0	1.0
98.1	89.3	8.1	1739.1	0.89	0.91	0.83
97.0	85.0	4.5	1738.8	0.83	0.82	0.67
94.9	80.1	3.7	1738.4	0.75	0.78	0.61
90.0	68.7	3.6	1737.6	0.57	0.62	0.39
76.5	54.6	2.8	1736.6	0.36	0.36	0.13
66.9	49.4	1.8	1736.0	0.23	0.27	0.07
12.3	13.0	2.5	1734.9	0	0	0
9.9	11.0	2.5	1735.0	0.02	0	0
6.5	7.3	2.4	1734.9	0	0	0
—[a]	50.4	—	1735.0	0.02	—	—

a) The copolymer prepared with $AlEt_{1.5}Cl_{1.5}$.[3]

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[1] F. Kamiyama, H. Matsuda, and H. Inagaki, *J. Phys. Chem.*, **71**, 4153 (1967).

[2] N. Ōi, K. Miyazaki, K. Moriguchi, and H. Shimada, *Kobunshi Kagaku*, **29**, 388 (1972).

[3] M. Hirooka, H. Yabuuchi, J. Iseki, and Y. Nakai, *J. Polym. Sci., Part A-1*, **6**, 1381 (1968).

meter which was calibrated against the absorption bands of atmospheric H_2O in 1800—1700 cm^{-1}.

Results and Discussion

The observed $\nu_{C=O}$ frequencies are summarized in Table 1. It is apparent that the C=O stretching mode of MA units regularly shifts to lower frequencies as the MA content decreases, and attains to a constant frequency in copolymers with low MA contents. This fact suggests that the peak positions of the carbonyl absorption bands are correlated to the sequence distributions of MA units in copolymers. Thus, the $\nu_{C=O}$ frequencies were plotted against P_{MM} and P_{MMM}, which are the probabilities for finding the MA–MA and MA–MA–MA linkages respectively in a chain. These probabilities were calculated for low-conversion copolymers from the feed compositions and the reactivity ratios for MA and ST, $r_{MA}=0.20$ and $r_{ST}=0.75$,[4] according to the equations in Ref. 5.

Figure 1 shows that $\nu_{C=O}$ is linearly proportional to P_{MM}. Thus, the following equation was used to calculate P_{MM} values in copolymers:

$$\nu C{=}O = aP_{MM} + bP_{MS}$$

In this equation, P_{MS} is the probability of finding the MA–ST linkage in a copolymer chain and the coefficients, a and b, represent the frequencies of the carbonyl bands for MA units in the MA–MA and MA–ST diads respectively. The a coefficient was evaluated from the spectrum of the MA homopolymer, and b, from the spectra of the copolymers with low MA contents, because the MA units are essentially isolated. As $P_{MM}+P_{MS}=1$, $a=1739.6$, and $b=1734.9$ in a benzene solution, the P_{MM} values of random copolymers can be determined by measuring the $\nu_{C=O}$ frequencies in a benzene solution and by using the following equation:

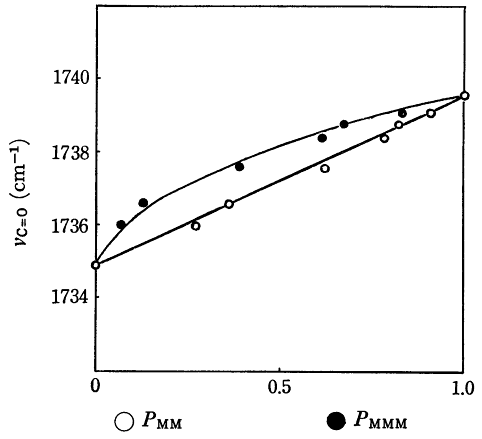

Fig. 1. The C=O stretching frequencies related to the probabilities of MA–MA and MA–MA–MA linkages in methyl acrylate(MA)–styrene copolymers.

$$P_{MM} = (\nu C{=}O - b)/(a-b) = (\nu C{=}O - 1734.9)/4.7$$

The measured P_{MM} values are in reasonably good agreement with the calculated values, as is shown in Table 1. Moreover, noteworthy that the measured P_{MM} value of the copolymer prepared with ethylaluminum sesquichloride is nearly zero; this fact supports the idea that such a copolymer has a highly alternating sequence.[3]

In conclusion, the carbonyl stretching mode in MA–ST copolymers is sensitive to the sequence environment and is, hence, useful for determining the sequence distribution of MA units.

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[4] T. Alfrey, Jr., E. Mers, and H. Mark, *J. Polym. Sci.*, **1**, 37 (1946).

[5] H. J. Harwood and W. M. Ritchey, *J. Polym. Sci., Part B*, **2**, 601 (1964).