

# Copolymerization of Zinc Methacrylate and Perfluoroalkyl Acrylate in Hydrocarbon Medium

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## SYNOPSIS

The copolymerization of zinc methacrylate (ZMA) and 2-(*N*-ethylperfluorooctanesulfonamide)ethyl acrylate (RFA) in benzene was studied as a model for the copolymerization of ZMA and RFA in synthetic rubber during the peroxide curing process (*in situ* copolymerization). To confirm copolymer formation from combination of the specified monomers bearing functional groups with different characteristics, experimental procedures to quantify unchanged monomers and two types of monomer units in the copolymer were established. As a result, it was ascertained that the copolymer composition was the same with that of the comonomer composition for an equimolar mixture of the monomers regardless of conversion. We can conclude that the composition of the copolymer resulting from the *in situ* copolymerization can be determined and the *in situ* copolymerization could be a novel method to modify the properties of rubber. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer alloys and blends have been utilized to improve the characteristics of polymer materials depending on their requirements.<sup>1,2</sup> Usually, polymer alloys and blends are advantageous over homopolymer and copolymer materials because of material design based on molecule structure and morphology. The polymer alloy and blend could also be applied to modify rubber.<sup>3</sup> Recently, techniques of morphology control for polymer alloys have been developed using various compatibilizers. On the other hand, a composite consisting of two types of polymers has been manufactured by polymerization of a monomer in the presence of a polymer, which is called *in situ* polymerization.<sup>4</sup> This technique has drawn attention to the obtaining of polymer composites from polymers which are not miscible with each other.

Although the high strength and abrasion resistance of rubber have been attained by polymer-

ization of zinc methacrylate (ZMA) in rubber,<sup>5-8</sup> the *in situ* copolymerization of two types of monomers has not been studied. We thought that *in situ* polymerization of two types of monomers having unlike characteristics could modify the properties of rubber over a wider range than can the polymerization of a single monomer. We chose ZMA and 2-(*N*-ethylperfluorooctanesulfonamide)ethyl acrylate (RFA) with the hope that modification using their copolymers for the high strength and abrasion resistance from the carboxylic salt in the ZMA unit and low friction and uncohesiveness from the perfluoro functional group in RFA would be successful. To this purpose, ZMA and RFA should be copolymerized through the *in situ* process. However, copolymerization studies of the combination of these monomers has not been done to our knowledge. Therefore, it was necessary to examine the effects of the medium on the copolymerization of ZMA and RFA, which are expected to have unlike solubilities in hydrocarbons including rubber. From these points of view, we copolymerized ZMA and RFA in benzene and determined the copolymerization reactivities based on the procedure developed.

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**Table I** Copolymerization of ZMA with RFA in Benzene at 60°C

Chemical	Weight (g)	Concentration (mol/L)
ZMA	1.02	0.534 <sup>a</sup>
RFA	4.36	0.534
AIBN	0.0316	0.0142

<sup>a</sup> Concentration of methacryloyl moiety.

## EXPERIMENTAL

### Materials

ZMA was R-20S grade supplied by Asada Chemicals Ind. Ltd. RFA was FX-13 grade supplied by Sumitomo 3M. Commercial 2,2-azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried on phosphorus pentoxide under vacuum. Benzene, methanol, acetone, and 35% hydrochloric acid were reagent-grade chemicals. A 10% *n*-hexane solution of trimethylsilyl diazomethane (TMS-diazomethane) was used as supplied.

### Polymerization

#### Copolymerization and Homopolymerization

Copolymerization was done in a 24 mL glass sealed tube using benzene as the solvent. The monomers and AIBN were weighed and admitted to the test tube at the prescribed concentration. The ampule was sealed under vacuum after deaeration using the freeze-and-thaw method. The copolymerization and homopolymerization were carried out in a thermostated bath at 60°C. Homopolymerization of each monomer was also done using benzene as the solvent for 70 min at 60°C.

#### Copolymer Composition

The copolymerization was carried out at the fixed comonomer composition shown in Table I. The copolymers were isolated from the respective copolymerization mixtures at different conversions based on the solubilities of the comonomer and the copolymer as summarized in Table II. The contents of the ampule were added to 10 mL of benzene and the supernatant was separated from the precipitate by a centrifuge. The precipitate was washed with benzene by stirring, and an additional supernatant was separated from the insoluble portion by the centrifuge again.

The supernatants were combined with the benzene used for washing the precipitate. A nonvolatile

**Table II** Solubilities of Monomers and Polymers

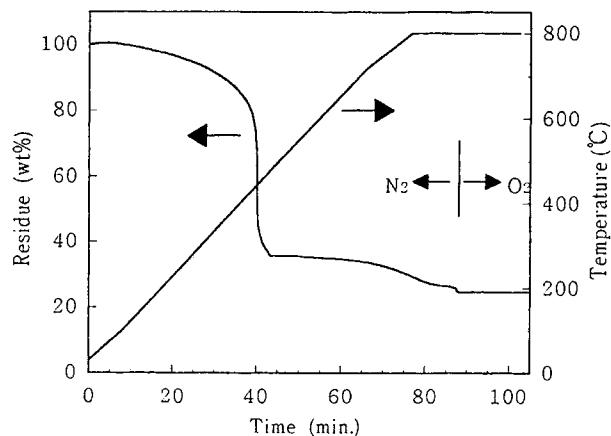
Monomer or Polymer	Solubility <sup>a</sup>		
	Benzene	Acetone	Water
ZMA	I	I	—
Poly(ZMA)	I	I	I
RFA	S	S	I
Poly(RFA)	I	I	I
MAA <sup>b</sup>	S	S	S
Poly(MAA)	I	I	S
ZMA-RFA copolymer	I	I	I
MAA-RFA copolymer	I	I	I

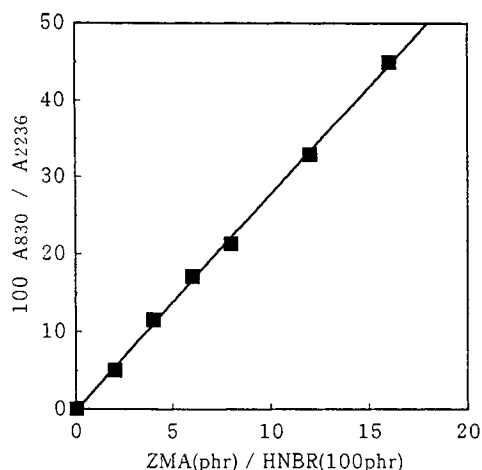
<sup>a</sup> I: insoluble; S: soluble.

<sup>b</sup> MAA = methacrylic acid.

component of the combined supernatant, which was obtained by evaporation of the benzene, was subjected to thermogravimetric analysis (TG) to quantify the pyrolytic residue of the nonvolatile component. The residual weight of TG from ZMA was separately obtained using monomeric ZMA. The content of ZMA in the supernatant was calculated from the residual weight of TG. The content of RFA was determined as the remaining nonvolatile fraction after subtraction of the ZMA amount.

The precipitate separated from the copolymerization mixture by the centrifuge was mixed with a known quantity of hydrogenated nitrile rubber (HNBR). The portion of the unchanged ZMA in the insoluble fraction was determined by FTIR spectroscopy using the intensity ratio of the absorptions at 2236 (C≡N stretching) and 830 cm<sup>-1</sup> (H—C=C deformation).<sup>9</sup> The calibration curve was obtained by measuring the intensities of the absorptions at 2236 and 830 cm<sup>-1</sup> of the mixtures of ZMA with HNBR at various ZMA contents. The total amount of ZMA in the copolymerization mix-

**Figure 1** TG thermogram of ZMA.



**Figure 2** A plot of ratio of absorbance at 830 to 2236  $\text{cm}^{-1}$  vs. content of ZMA in HNBR.

ture was obtained as the summation of the ZMA content in the precipitate determined by FTIR spectroscopy and the ZMA content of the supernatant.

#### Transformation of ZMA Unit to Methyl Methacrylate Unit

The benzene insoluble fraction (2 g) was stirred with 2 mL of 35% hydrochloric acid in 70 mL of acetone. Because an excess amount of hydrochloric acid was used relative to ZMA and the ZMA unit, they could be converted to methacrylic acid and the methacrylic acid unit, respectively. The precipitate was filtered and washed with acetone and water. Separately prepared poly(ZMA) and poly(RFA) were also treated in a similar manner with hydrochloric acid. The polymer, 0.4 g, dissolved in benzene containing 20 vol % methanol was allowed to react with 0.5 mL of TMS-diazomethane with stirring for 1 day, and the polymer sample was washed with benzene. The polymer from the poly(ZMA) did not exhibit an absorption at  $1738 \text{ cm}^{-1}$ , whereas no change was observed in the spectrum of the RFA homopolymer after treatment with the hydrochloric acid and subsequent reaction with the diazomethane.

#### Measurements

A Seiko Electron Industries Ltd. TG/DTA300 was used for the TG. About 10 mg of sample was heated in nitrogen gas over the temperature range from 30 to  $800^\circ\text{C}$  at the heating rate of  $10^\circ\text{C}/\text{min}$  followed by heating in an oxygen atmosphere at  $800^\circ\text{C}$ . A Perkin-Elmer FTIR 1600 was used to measure the Fourier transformed infrared spectra (FTIR). The

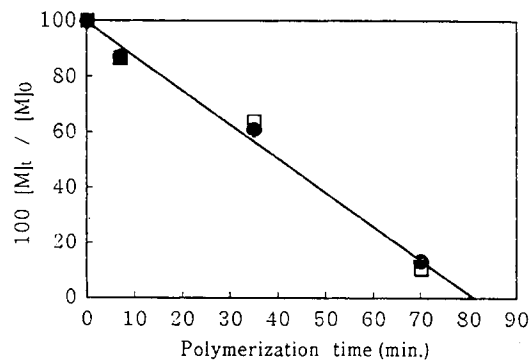
samples were spread on a NaCl plate for FTIR measurement.

## RESULTS AND DISCUSSION

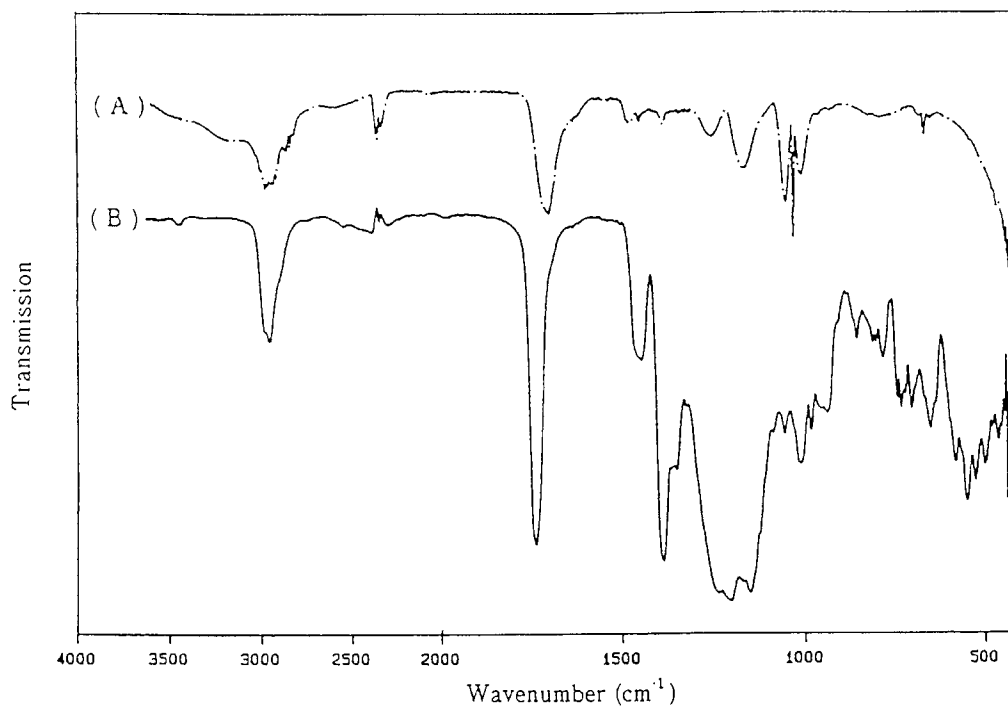
The copolymerization of ZMA and RFA in benzene was carried out at  $60^\circ\text{C}$ . The composition of the copolymerization mixture is shown in Table I. After a certain copolymerization time, the contents of the ampule were poured into a large amount of benzene. The monomer and the respective homopolymers exhibited different solubilities as summarized in Table II.

The content of ZMA in the benzene solution was determined, because ZMA that is insoluble in benzene might be solubilized in the benzene solution containing RFA. The content of ZMA in the benzene-soluble fraction was determined by TG. The TG thermogram of the monomer ZMA illustrated in Figure 1 shows that no decrease in weight occurs after heating for 90 min and that the pyrolytic residue is 25 wt % of the initial weight. The weight ratio of the pyrolytic residue remained constant regardless of the quantity of ZMA. As RFA yielded no pyrolytic residue, the ZMA content in the soluble component of the copolymerization mixture was calculated from the quantity of the residue. The content of RFA was determined as the remaining nonvolatile fraction after subtraction of the ZMA amount.

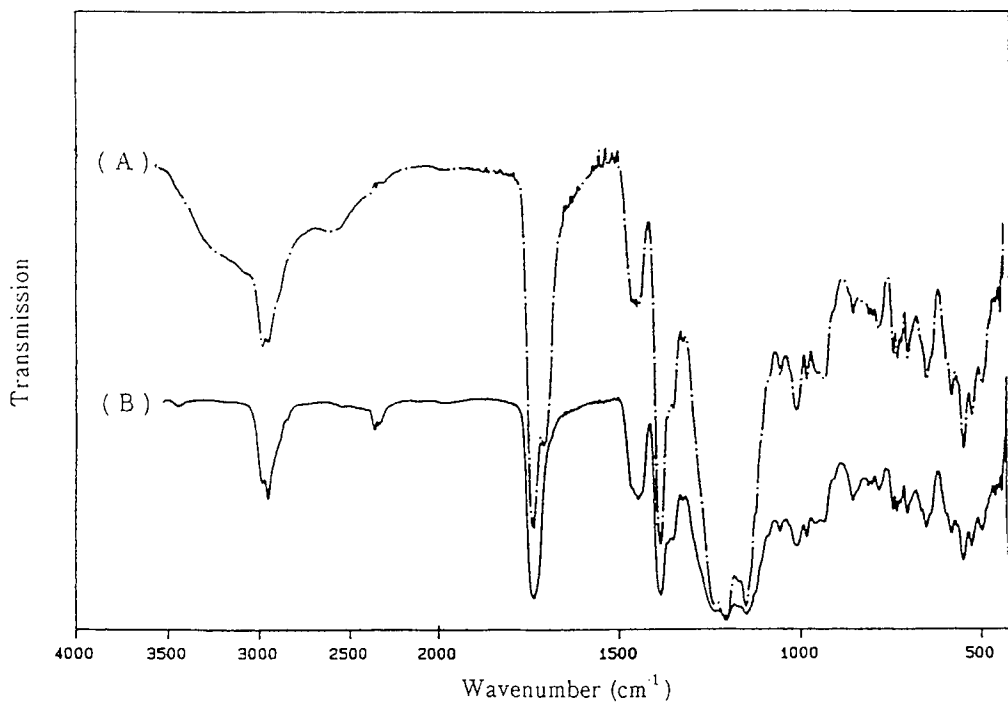
Because most of the ZMA was involved in the insoluble fraction after centrifuge, the content of ZMA separated from the ZMA unit in the copolymer was determined using FTIR spectroscopy. For this purpose, a relationship between the intensity of the characteristic absorption band due to ZMA such as  $830 \text{ cm}^{-1}$  relative to a reference absorption band due



**Figure 3** Consumption of (□) ZMA and (●) RFA in copolymerization initiated with AIBN in benzene at  $60^\circ\text{C}$ ;  $[\text{ZMA}] = 0.534 \text{ mol/L}$ ;  $[\text{RFA}] = 0.534 \text{ mol/L}$ ;  $[\text{AIBN}] = 0.0142 \text{ mol/L}$ .



**Figure 4** FTIR spectra of (A) poly(ZMA) and (B) poly(RFA) after treatment with the hydrochloric acid.



**Figure 5** FTIR spectra of the copolymer obtained by copolymerization after treatment with the (A) hydrochloric acid and (B) the copolymer after treatment with the hydrochloric acid followed by methylation.

to HNBR such as  $2236\text{ cm}^{-1}$  has to be obtained. The calibration curve is shown in Figure 2. We confirmed that ZMA was quantified within several percent accuracy for a known quantity of ZMA mixed with HNBR. Therefore, the contents of ZMA in the insoluble fractions were determined by FTIR.

A change in comonomer composition was monitored by TG and IR spectroscopy (Fig. 3). It is not plausible that ZMA and RFA are consumed by individual homopolymerizations with the same rate. However, the copolymer formation of ZMA and RFA should be confirmed.

Each benzene insoluble fraction of the copolymerization and the homopolymerization was treated with hydrochloric acid followed by methylation. As a result, the copolymerization of ZMA with RFA was unambiguously confirmed.

The infrared spectrum of the homopolymers of ZMA and RFA after the treatment with hydrochloric acid are depicted in Figure 4. The absorption around  $1738\text{ cm}^{-1}$  of RFA is ascribable to the carbonyl group of the RFA homopolymer and the characteristic absorption around  $1708\text{ cm}^{-1}$  is assigned to the carbonyl group of the methacrylic acid homopolymer. After the treatment with hydrochloric acid, the copolymer exhibits two types of absorptions due to the carbonyl stretching at  $1708$  and  $1738\text{ cm}^{-1}$  as can be seen in Figure 5. Furthermore, the absorption around  $1708\text{ cm}^{-1}$  disappeared after methylation with the diazomethane. Therefore, it was confirmed that RFA and methacrylic acid units are involved in the copolymer. The formation of a homogeneous copolymer may be due to the amphiphilic character of RFA, which facilitates mixing of the comonomer and solvent.

Compositions of the copolymers were determined on the basis of the composition of the comonomer, as summarized in Table III. Apparently, ZMA and RFA were consumed at the same rate, indicating that the copolymers of the same composition with the comonomer were produced.

## CONCLUSIONS

We copolymerized two types of monomers with different characteristics in hydrocarbon medium. The monomers used were ZMA and RFA, which were expected to modify effectively with special rubber properties by *in situ* copolymerization. We developed the procedure to monitor monomer consumption and determined the composition of the copolymer. Although the copolymerization apparently proceeded in a heterogeneous system because of the different monomer solubilities, the copolymers consisting of the same composition were produced re-

**Table III** Composition of ZMA-RFA Copolymer at Different Stages

Polymerization Time (min)	Comonomer Composition (mol %)		[ZMA] <sup>a</sup> /[RFA] in Copolymer (Molar Ratio)
	[ZMA] <sup>a</sup>	[RFA]	
7	87	87	1.00
35	64	61	0.95
70	10	13	1.03

<sup>a</sup> Concentration of methacryloyl moiety.

gardless of conversion. Therefore, we could design the copolymer for modification of rubber by adjusting the composition of the copolymer.

Actually, we obtained a rubber that had over 35 MPa tensile strength by *in situ* copolymerization of these monomers in HNBR. Because HNBR compounded with carbon black shows the tensile strength of 20–30 MPa, the effect of *in situ* copolymerization is apparently observed. This rubber showed about 60% lower surface friction than did a rubber obtained by *in situ* polymerization of ZMA in HNBR. We will report the properties of the modified rubber in detail. Further work is required to understand the reacting behavior in rubber as a more complicated system for revealing the mechanism of these modified functions.

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