Copolymerization of Zinc Methacrylate and Perfluoroalkyl Acrylates in Different Solvents

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ABSTRACT: The copolymerizations of zinc dimethacrylate (ZMA) and 2-(*N*-ethylperfluorooctanesulfonamide)ethyl acrylate (RfSA) in various solvents were carried out in relation to the copolymerization of ZMA and RfSA in a synthetic rubber during the peroxide curing process (*in situ* copolymerization). The ZMA–RfSA copolymerization initiated with 2,2′-azobisisobutyronitrile at an equimolar mixture of the monomers yielded a copolymer of which the composition was almost the same with that of the comonomer, regardless of the solvent used. It was considered that the sulfonamido group in monomeric RfSA and the copolymer of RfSA specifically improves the miscibility of RfSA with ZMA. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1499–1504, 1999

Key words: zinc dimethacrylate; fluorine-containing monomer; radical copolymerization; solution copolymerization; sulfonamido group

INTRODUCTION

Denaturation of polymeric materials by mixing with a monomer that can be allowed to polymerize has been studied from different points of view such as grafting on the polymer chain and interpenetrating polymer network formation via *in situ* polymerization.[1] The *in situ* polymerization is advantageous over mixing polymeric materials because polymer is mixed with a monomer much easier than with other polymers.

Metal acrylates and methacrylates have been employed for reinforcement by grafting for the denaturation of elastomers.[2,3] It has been considered that intermolecular interaction between the metal ion and carboxylate group is primarily important for the reinforcement. Furthermore, a nano-composite material with features of high strength, toughness, and abrasion resistance can

be formed by *in situ* polymerization of zinc dimethacrylate (ZMA) in hydrogenated nitrile butadiene rubber (HNBR) during peroxide vulcanization.[4] The *in situ* polymerization of ZMA has shown that about 80% of the initial amount of ZMA diffuses into the HNBR matrix, followed by polymerization during the peroxide vulcanization, and the remaining 20% of ZMA yields the poly(ZMA) as branching of the graft copolymer on HNBR.[5] The *in situ* copolymerization of two types of monomers having unlike characteristics could modify the properties of rubber over a considerably wider range in comparison with the *in situ* polymerization of a single monomer.

We chose ZMA and 2-(*N*-ethylperfluorooctanesulfonamide)ethyl acrylate (RfSA) as the monomers for the *in situ* copolymerization in HNBR during the peroxide vulcanization.[6] As a result, superior tensile strength, which was about 35 MPa, and about 60% lower surface friction than that obtained by *in situ* polymerization of ZMA alone in HNBR have been confirmed. The enhanced strength and low friction are considered to

$$CF_3-(CF_2)_7-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{C_2H_5}{\underset{}{N}}-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-CH=CH_2$$

RfSA

$$CF_3-(CF_2)_7-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-\overset{CH_3}{\underset{}{C}}=CH_2$$

RfM

$$CF_3-(CF_2)_7-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-CH=CH_2$$

RfA

Figure 1 Fluorine-containing monomers.

arise from the carboxylic salt in the ZMA unit and the perfluoroalkyl group in the RfSA unit, respectively.

We copolymerized an equimolar mixture of these monomers in benzene as hydrocarbon medium, as already reported.[7] The copolymers consisting of almost the same composition with the comonomer are produced regardless of conversion, in spite of the apparently heterogeneous copolymerization system arising from different monomer solubilities to the polymerization mixture. However, to obtain the elastomers with satisfactory balanced characteristics by the *in situ* copolymerization, further study of the copolymerization of the two types of the monomers exhibiting desired characteristics seems to be required.

In the present work, we carried out the copolymerizations of ZMA and RfSA at various comonomer compositions, and the copolymerizations of 2-perfluorooctylethyl acrylate (RfA) and 2-perfluorooctylethyl methacrylate (RfM) with ZMA were also run in different solvents in relation to the medium effect on the *in situ* copolymerization.

EXPERIMENTATION

Materials

ZMA (R-20S grade) was supplied from Asada Chemicals Ind. Ltd. RfSA was supplied from Sumitomo 3M as FX-13 grade. RfA and RfM were 17F and 17FM grade supplied from Osaka Organic Chemical Ltd., respectively. Commercial 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried on phosphorus pentoxide under vacuum. Benzene, *N,N*-dimethylformamide (DMF), and methanol were reagent

grade chemicals. HNBR were supplied by Nippon Zeon Co. Ltd., as Zetpol 2020 grade, which contains 36% ACN and 10% double bond.

Copolymerization and Homopolymerization

Copolymerization was done in a 24-mL glass-sealed tube using benzene, DMF, or methanol as the solvent, and the total concentration of monomers and AIBN concentration were 1.07 mol/L and 0.014 mol/L, respectively. The concentration or content of ZMA in the comonomer and copolymer were given with respect to the methacryloyl moiety of ZMA. The monomers and AIBN were weighed and admitted to the ampoule, where the contents were degassed by the freeze and thaw method and sealed under vacuum. The copolymerization was carried out in a thermostated bath at 60°C. The homopolymerization of each monomer was also done using benzene as the solvent for 70 min at 60°C.

Copolymer Composition

After the copolymerization for a prescribed time, the contents of the ampoule were added to 40 mL of the solvent used for copolymerization, and the precipitate was filtered by a sintered glass filter. After washing with the solvent with stirring, a nonvolatile residue in the combined filtrate, which was obtained by evaporation of the solvent from the filtrate, was subjected to thermogravimetric analysis (TGA) to quantify the pyrolytic residue.

Table I shows the residual weight of monomeric ZMA relative to the initial weight measured by TGA under different conditions illustrated in Figure 2. About one-third of the initial weight was found to remain as the residue after TGA. According to this procedure, a small amount of ZMA dissolved in the filtrate was calculated from the nonvolatile fraction of the filtrate based

Table I   Residual Weight Ratio of ZMA for Calibration by TGA under Different Conditions

System	Heating Pattern	Residual ZMA (wt/wt)
ZMA	A	0.304
ZMA	B	0.301
ZMA/benzene	A	0.319
ZMA/methanol	A	0.313
ZMA/DMF	B	0.391

Figure 2 Heating pattern for TGA.

on the TGA residual weight. The content of the fluoromonomer was determined by subtraction of the small amount of ZMA from the total amount of the nonvolatile fraction of the filtrate.

A colorless product separated from the copolymerization mixture by filtration was mixed with the acetone solution of a known quantity of HNBR to estimate the monomers remaining in the product by infrared analysis (FTIR). The content of the unchanged ZMA in the insoluble fraction was determined by FTIR spectroscopy using the intensity ratio of the absorptions at 830 cm^{-1} (H—C=C deformation) arising from ZMA, and 2236 cm^{-1} (C≡N stretching) arising from HNBR. A calibration curve for the quantification of ZMA was obtained by measuring the intensities of the absorptions at 830 cm^{-1} and 2236 cm^{-1} of HNBR containing known amounts of ZMA. The total amount of unchanged ZMA in the copolymerization mixture was obtained as the summation of the ZMA contents in the precipitate and the filtrate.

Measurements

A Seiko TG/DTA320 was used for TGA; about 10 mg of sample was heated at the heating patterns of TGA measurement shown in Figure 2. A Seiko DSC200 was used to measure the beginning temperature of the main endothermic peak (T_e). About 10 mg of sample was heated in a nitrogen atmosphere from 30 to 150°C at the heating rate of 2°C/min. FTIR spectra were recorded on a JASCO FTIR 230. The sample solutions were spread on and bound between KBr plates.

RESULTS AND DISCUSSION

Copolymer Composition at Different Conversions

The composition of the ZMA–RfSA copolymer was determined from the amounts of the unreacted

monomers according to the prescribed procedure.[8] For example, the copolymer obtained from the comonomer consisting 30 mol % of ZMA and 70 mol % of RfSA after copolymerization in benzene for 70 min, from which the filtrate, 0.7132 g, and precipitate, 6.5658 g, were obtained, was subjected to the determination of the composition. The amounts of unchanged ZMA determined by TGA analysis and by FTIR analysis were 3.14 wt % of the filtrate and 3.06 wt % of the precipitate, respectively. The content of ZMA determined by the different procedures agreed satisfactory. Consequently, 96.9% of the filtrate would correspond to the unchanged RfSA, and FTIR spectroscopy confirmed that the precipitate did not contain the monomeric RfSA.

Comonomer–copolymer composition curves with respect to the methacryloyl moiety of ZMA, and the copolymer of ZMA and RfSA are shown in Figure 3 where f_1 and F_1 denote comonomer and copolymer compositions given by the following equations, respectively.

$$f_1 = [ZMA]/([ZMA] + [RfSA])$$

$$F_1 = d[ZMA]/(d[ZMA] + d[RfSA])$$

The copolymers isolated after the copolymerization for 70 min at high conversions of both monomers, of which the range were from 57 to 90%, were found to contain almost the same amount of the ZMA unit with that of the ZMA in the comonomer. The compositions of the copolymers obtained after copolymerization for 7 min at low conversions of at least one of the monomers, of which the ranges were from 13 to 28%, did not

Figure 3 Relationship between ZMA content in comonomer (f_1) and copolymer (F_1) for ZMA–RfSA copolymerization for 7 min (○) and 70 min (■) at 60°C.

Figure 4 Relationship between beginning temperature of main endothermic peak (T_e) and F_1 of ZMA–RfSA copolymer after copolymerization for 70 min at 60°C.

Figure 5 DSC chart of the copolymer after copolymerization in benzene at 60°C for 7 min and 70 min; [ZMA] : [RfSA] = 9 : 1 (molar ratio).

fit to the copolymer composition curve at the high conversion except for the copolymerization of an equimolar mixture of ZMA and RfSA.

In the previous study of the copolymerizations of ZMA with methyl methacrylate (MMA) and styrene (St), the composition relations at a low conversion were expressed by the theoretical curve calculated from $r_1 < 1$ and $r_2 < 1$.[8] The copolymer composition curve obtained on the basis of the copolymer compositions after copolymerization for 70 min indicates that r_1 and r_2 are close to unity. In the case of the copolymerization of ZMA and RfSA shown in Figure 3, the contents of ZMA in the copolymers at low conversions were found to be greater than those at high conversions, whereas the copolymer composition at an equimolar mixture of ZMA and RfSA remained the same composition with that of the comonomer. Consequently, the copolymer composition curves in the range of $f_1 \leq 0.5$ may also be explained by $r_1 < 1$ and $r_2 < 1$. The composition plot in the range of $f_1 > 0.5$ at the low conversions predicts $r_1 > 1$ and $r_2 < 1$, because the copolymers isolated contained larger amounts of the ZMA unit than ZMA in the comonomers, as shown in Figure 3.

To characterize the copolymers isolated, the temperature of the endothermic peak in the DSC was measured. The T_e of the copolymers obtained after copolymerization for 70 min was found to change from 47 to 114°C, as shown in Figure 4. It is noted that these temperatures are the T_e of the poly(RfSA) and the poly(ZMA), respectively. However, the T_e exhibits complicated dependence on comonomer composition and conversion. For ex-

ample, the T_e at $f_1 = 0.9$, shown in Figure 5, changed from 85°C for the copolymer (70 min) to 108°C for that obtained at 7 min. Apparently, the second endothermic peak for the copolymer obtained at 70 min is close to the T_e for the copolymer isolated at the low conversion.

Effects of the Sulfonamido Group

The copolymerization results of ZMA with the fluorine-containing monomers at equimolar mixtures in benzene are shown in Figures 6 and 7. Comparison of the copolymerization rates of ZMA and the fluorine-containing monomers could predict the copolymer composition. It was anticipated from the similar copolymerization rates that the compositions of the ZMA–RfSA copolymers are almost the same with the compositions of the comonomer, irrespective of conversion. RfM was copolymerized almost quantitatively after

Figure 6 Conversion of ZMA in copolymerization of ZMA–RfSA (■), ZMA–RfM (▲), and ZMA–RfA (●) initiated with AIBN in benzene at 60°C: [ZMA] = 0.534 mol/L, [Rf] = 0.534 mol/L, [AIBN] = 0.0142 mol/L.

Figure 7 Conversion of fluoromonomer in copolymerization of ZMA–RfSA (■), ZMA–RfM (▲), and ZMA–RfA (●) initiated with AIBN in benzene at 60°C: [ZMA] = 0.534 mol/L, [Rf] = 0.534 mol/L, [AIBN] = 0.0142 mol/L.

the copolymerization for 35 min. The conversion of RfM increased with an increase of copolymerization time from 35 to 70 min. The copolymerization of RfA seems to be faster than that of ZMA because of the significantly higher conversion for RfA after the copolymerization for 35 min. Actually, only ZMA was consumed during the copolymerization for a longer period than 35 min.

In the copolymerization of methacrylic acid with *n*-butyl acrylate and *n*-butyl methacrylate, the acrylic ester was incorporated more than methacrylic ester in the copolymer.[9] Similarly, comparison of the composition of ZMA–RfM copolymer with that of ZMA–RfA copolymer after copolymerization for 35 min revealed that RfA was incorporated more than RfM in the copolymer. These copolymerization systems of ZMA with the fluorine-containing monomers were heterogeneous because only a small amount of ZMA can be dissolved in copolymerization mixtures. It is quite natural to presume that heterogeneity of the copolymerization system influences the copolymerization behavior as well as the monomer reactivity ratios.

On the basis of these findings, the copolymerization behaviors are deduced as follows. In the early stage of the copolymerization of the ZMA–RfA system, RfA was consumed predominantly, as shown in Figures 6 and 7, because of a solubility concentration of RfA rather than that of ZMA in the solvent used. According to the proceeding of the copolymerization, the content of dissolved ZMA was considered to increase as the RfA was consumed. Actually, ZMA polymerizes alone in

the absence of RfA at the final stage of the copolymerization. The copolymerization behavior of the ZMA–RfM system was described in almost the same manner as for the ZMA–RfA system. However, the compositions of the copolymers at the low conversion were not as different from the comonomer composition; the ZMA homopolymerization after exhaustion of RfM could undergo a longer period than that for the ZMA–RfA system.

In the ZMA–RfSA system, the reason why the copolymer composition is similar to that of the monomer mixture irrespective of conversion could be explained by a higher miscibility of ZMA in the RfSA–benzene solution and a slower homopolymerization rate of RfSA than that of ZMA. Probably the sulfonamido group in RfSA influenced an increase of the amount of ZMA in the homogeneous solution.

The effect of the sulfonamido group on copolymerization reactivity would be affected by the polarity of the solvent employed. We carried out the copolymerizations of the equimolar mixture of these monomers in benzene, methanol, and *N,N*-dimethylformamide. The results of the copolymerization at low conversions are summarized in Figure 8. The ZMA–RfSA system yielded the copolymer of which the composition remained almost the same with the comonomer composition, irrespective of the polarity of the solvent. The ZMA–RfA and ZMA–RfM copolymers exhibited a similar copolymer composition to the comonomer composition at the copolymerization in benzene. Although the ZMA–RfA and ZMA–RfM copolymers obtained in DMF are found to contain more than 30 mol % of the ZMA unit, the copolymer-

Figure 8 The copolymerization results of ZMA with the fluorine-containing monomers at equimolar mixtures in benzene, methanol, and DMF at 60°C for 7 min.

ization in methanol yielded the corresponding copolymer where the ZMA content is less than 10 mol %. In the ZMA–RfA and ZMA–RfM systems, the copolymer compositions were changed from the comonomer composition, depending on the solvent.

Therefore, it was considered that the copolymerizations of ZMA with the fluorine-containing monomers without the sulfonamido group were influenced not only the reactivity of the monomers but also the polarity of the polymerization medium. The sulfonamido group in RfSA and the copolymer of RfSA could enhance the miscibility of RfSA with ZMA to yield the comonomer mixture, leading to the copolymer consisting of almost the same content of both monomer units. The *N,N*-disubstituted sulfonamido group of RfSA seems to be an appropriate constitution to improve the miscibility with ZMA.

In the case of the *in situ* copolymerization of ZMA and RfSA in HNBR, the copolymerizations proceeded without phase separation of RfSA from the matrix.[6] The sulfonamido group of RfSA is expected to play an important role to attain these results, which are preferable for improvement of the characteristic of the rubber.

CONCLUSIONS

The copolymerization of ZMA and fluorine-containing acrylic or methacrylic monomers were studied in relation to the copolymerization of ZMA and RfSA in a synthetic rubber during the peroxide curing process (*in situ* copolymerization). The copolymerization initiated with AIBN has led to the following conclusions. The copolymerization behavior of the ZMA and RfSA seems to be different in the ranges of $f_1 < 0.5$ and $f_1 > 0.5$. The compositions of the ZMA–RfSA copolymer at an equimolar mixture of the monomers were almost the same with the composition of the comonomer, regardless of the conversion and polarity of the solvent. It was considered that the sulfonamido group in RfSA and the copolymer of RfSA increase the miscibility with ZMA.

REFERENCES

1. Utracki, L. A. Polymer Alloys and Blends; Hanser Publishers: New York, 1989; Japanese version by Nishi, T. Tokyo Kagakudozin 1991.
2. Heyes, R. A.; Conard, W. R. Jpn Kokai S59-149938, The Firestone Tire & Rubber Company, 1984.
3. Araki, J.; Tamura, M.; Naka, T. Jpn Kokai H1-146935, Honda Technical Research Center, Ltd., 1987.
4. Saito, Y.; Fujino, A.; Ikeda, A. SAE Tech Pap Ser (Soc Automot Eng) 1989, SAE-890359, 13.
5. Nomura, A.; Takano, J.; Toyoda, A.; Saito, Y. J Soc Rubber Ind Jpn 1993, 66, 830.
6. Ikeda, T.; Sakurai, S.; Nakano, K.; Yamada, B.; Okamoto, T. J Soc Rubber Ind Jpn 1996, 69, 423.
7. Ikeda, T.; Sakurai, S.; Nakano, K.; Yamada, B. J Appl Polym Sci 1996, 59, 781.
8. Yamada, B.; Yoneno, H.; Otu, T. J Chem Soc Jpn 1976, 6, 988.
9. Paxton, T. R. J Polym Sci 1963, B1, 73.