

Chemistry in Mega-gravity: Preparation of Molecular-scaled Graded Materials from Radical Copolymerization

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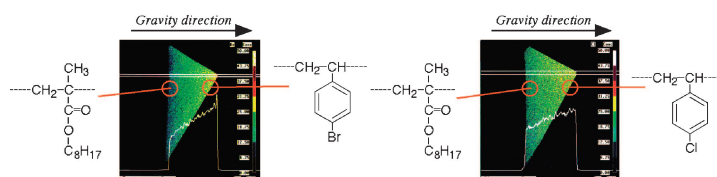
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(Received November 13, 2007; CL-071260; E-mail: ihara@kumamoto-u.ac.jp)

A molecular-scaled graded structure has been created by direct copolymerization of a monomer–monomer mixed system by using ultra-strong gravitational field.



REPRINTED FROM

**Chemistry
Letters**

Vol.37 No.2 2008 p.200–201

CMLTAG
February 5, 2008

The Chemical Society of Japan

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The molecular-graded structures have been realized through direct copolymerization of halogenated styrene and 2-ethylhexyl methacrylate under ultra-strong gravitational field. The graded structures were clearly confirmed by EPMA and NMR spectroscopy.

Functionally graded materials (FGMs) showing compositions and/or functions varying continuously or step-wisely have become known since Bever and Duwez predicted their potentiality as functional materials.^{1,2} FGMs have attractive potential for various industrial purposes such as materials for space systems, power transmission, and distribution systems, optical fiber, etc. Mostly inorganic FGMs are well known² but recently, FGMs have been realized for binary polymer blends. For example, a dissolution and diffusion method was developed for blends of poly(vinyl chloride)/poly(methyl methacrylate)³ and polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide).⁴ A coating method was applied for a THF solution from the blends of poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate)/poly(vinylidene fluoride-co-hexafluoroacetone).⁵ However, these methods were based on step-wise treatment and therefore a molecular-scaled graded structure cannot be produced. Despite many reports on FGM preparation from polymer blends, there is almost no report on FGM preparation from copolymerization of a monomer/monomer mixture, even though it would be a very useful approach for creating FGMs.

In this communication, we demonstrate the first example of molecular-scaled FGM preparation through copolymerization of a monomer/monomer mixture. To accomplish our purpose, we focused on carrying out copolymerization under a mega-gravity field in a 10^6 G level although there have been only a few reports of copolymerization under weak gravitational fields (10^3 – 10^4 G level).^{6,7} Recently, we succeeded in building up a mega gravity generator with jet power, which allowed sedimentation at an atomic level in metal alloys at high temperatures.⁸ This gravity is stronger than in the surface gravity on a white dwarf. Here, if two kinds of monomers having different molecular density (d) are exposed to a mega-gravity field and then the polymerization is initiated, it is expected that copolymerization may produce a molecularly graded structure in the monomer composition because of prior sedimentation of a heavier monomer. On the basis of this expectation, we selected halogenated styrene ($M_w = 183.05$, $d = 1.41$ in *p*-bromostyrene) as a heavy monomer and 2-ethylhexyl methacrylate ($M_w = 198.30$, $d = 0.89$) as a light monomer and polymerized them, and painstakingly developed a new mega-gravity generator that was usable at relatively lower temperatures such as 80–100 °C.⁹

The first copolymerization was carried out using a one-to-one mixture of *p*-bromostyrene (BrSt) and 2-ethylhexyl methacrylate (EHMA). 110 μ L of the monomers and 0.1 wt % of benzoyl peroxide (BPO) as a radical initiator were enclosed in a stainless-steel capsule (5 mm i.d. \times 10 mm) at room temperature and then placed at 100 °C for 24 h under 80×10^4 G generated by 14.3×10^4 rpm in our gravity generator.

Figure 1a shows the EPMA photomapping image¹⁰ for the polished surface of the resultant solid prepared under 80×10^4 G generated by 14.3×10^4 rpm. The composition profile of bromide showed distinctly that the amount of bromide increased continuously in the direction of the gravitational field. No similar composition change was observed in the sample prepared under 2×10^4 G generated by 2.23×10^4 rpm as shown in Figure 1c. Of course, an experiment under 1 G did not show any composition change. These results indicate that only an ultra-strong gravitational field can induce selective sedimentation for a heavy atom-containing moiety.

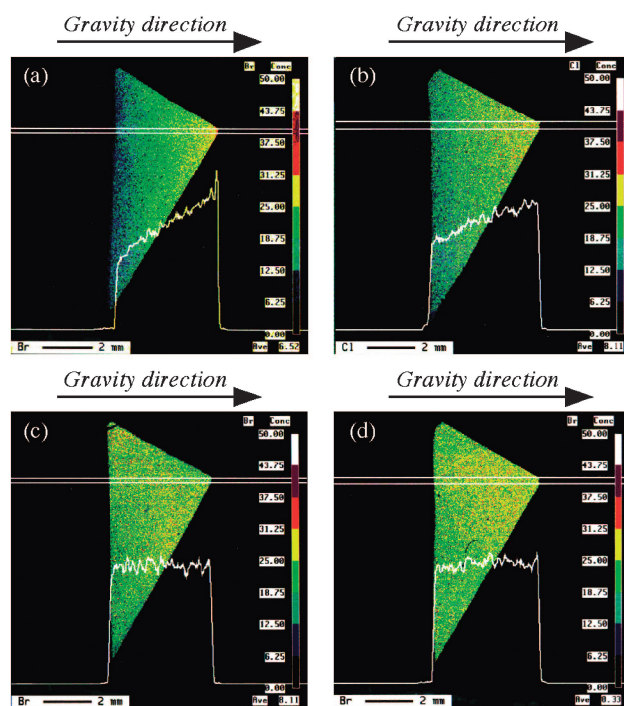


Figure 1. EPMA photomapping images of the resultant copolymers prepared with (a), (c) BrSt–EHMA, (b) ClSt–EHMA, and (d) BrSt–St. The monomer mixtures (1:1) with BPO were exposed at 100 °C for 24 h under (a), (b), and (d) 80×10^4 G and (c) 2×10^4 G.

Table 1. Composition^a of the resultant copolymers prepared under strong gravity

	BrSt–EHMA				ClSt–EHMA	
	80 × 10 ⁴ G		2 × 10 ⁴ G		80 × 10 ⁴ G	
	BrSt /%	EHMA /%	BrSt /%	EHMA /%	ClSt /%	EHMA /%
Portion 1	35	65	49	51	42	58
Portion 2	43	57	51	49	48	52
Portion 3	52	48	50	50	51	49
Portion 4	62	38	50	50	51	49
Portion 5	65	35	50	50	54	46

^aEach composition was determined by the proton ratio assigned by the proton signals due to the phenyl (in BrSt or ClSt) and diethylhexyl (in EHMA) groups. Solvent: CDCl₃.

¹H NMR spectroscopy¹⁰ provided the following important information: firstly, there was no signal based on the vinyl groups in the whole of the obtained bulk solid while the vinyl groups are found at 5.7 and 5.2 ppm in BrSt, and 6.1 and 5.5 ppm in EHMA in CDCl₃. This indicates that both monomers were almost completely polymerized by the present procedure. Supporting this, SEC analysis¹⁰ showed that there was no trace of each monomer and that the average molecular weights (M_w) were estimated to be 2×10^5 and 7×10^5 in the resultant polymers prepared under 80×10^4 and 2×10^4 G, respectively although we are still investigating how the gravitational field influences to the degree of polymerization. Secondly, the NMR analysis clarified the formation of a graded structure in the monomer compositions as summarized in Table 1. This analysis was carried out by the following procedure: the capsule was cut at a plane with a diamond cutter and then the resultant solid was divided into five portions according to the direction of the gravitational field. Each portion (copolymer) was dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy. Each NMR spectrum included signals due to the protons of poly(BrSt) and poly(EHMA) but their compositions were different in each portion. As is clear in Table 1, the sample prepared under 80×10^4 G showed a distinct monomer composition change in the direction of the gravitational field but the composition was almost constant in the copolymer prepared under 2×10^4 G. Therefore, it can be concluded briefly that mega-level gravity can induce molecular sedimentation to lead to a molecularly graded structure.

In order to approach the mechanism of molecular sedimentation, we followed further copolymerization for several interesting combinations including mixed systems composed of *p*-chlorostyrene (ClSt) and EHMA, styrene (St) and EHMA, and BrSt and St. Their *d* ratios were 1.09/0.89, 0.90/0.89, and 1.41/0.90, respectively. As a result, the ClSt–EHMA mixed system showed a graded structure (Figure 1b) and composition change (Table 1) in the direction of the gravitational field but no graded structure was observed in the St–EHMA mixed system even under 80×10^4 G. These results are reasonably understandable from their *d* values. However, a confusing result was encountered in the BrSt–St mixed system because there was no graded structure (Figure 1d) regardless of the big difference in the *d* values. This indicates that the density (molecular weight) difference is not a sufficient condition to create a graded structure in copolymerization and therefore other factors should be considered. Here, we

assume that molecular sedimentation can occur only for large molecules such as oligomers (or polymers) but not for monomers. On the basis of this assumption, the monomer reactivity ratios may be an important factor, especially at the initial stage of polymerization, because the monomer reactivity ratio of BrSt for alkyl acrylate is much larger ($r_1/r_2 = 1.10/0.40$ in methyl methacrylate) than for St ($r_1/r_2 = 0.99/0.70$).¹¹ Another answer may be due to molecular miscibility between monomers. Even mega-level gravity cannot be overcome for selective sedimentation in a monomer–monomer mixed system.

In conclusion, we have realized a novel method to prepare the binary molecular-scaled graded materials from direct copolymerization of a monomer–monomer mixed system by using mega-gravity field generator. This was only achieved under an ultra-strong gravitational field such as a mega-G level. The graded structure was confirmed both by a surface analysis with EPMA and a bulk analysis with NMR spectroscopy, and the composition changed continuously at a molecular level in the direction of the gravitational field. The exact mechanism of molecular sedimentation has not been specified but at least molecular density (weight) must be one essential factor.

This research was partially supported by the Ministry of Education, Culture, Sport, Science and Technology, Grant-in-Aid, and Kumamoto University 21st Century COE Program of Pulsed Power Science.

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