

Studies on the Light-Focusing Plastic Rod. IX. Chemical Composition of the Copolymer Rod- Diethylene Glycol Bis(allyl Carbonate) with 2,2,3,3- Tetrafluoropropyl Methacrylate

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Synopsis

For the preparation of the light-focusing plastic rod (LFR) a gel rod of partially polymerized diethylene glycol bis(allyl carbonate) (CR-39) was immersed in 2,2,3,3-tetrafluoropropyl methacrylate (4FMA) followed by heat treatment under nitrogen. Variations in the chemical composition in this process indicated the following mode of copolymerization: copolymerization of 4FMA with the allylic group in the gel rod occurs to some extent in the immersion process, but a significant amount of either 4FMA or CR-39 remains in the rod. Under heat treatment, these monomers copolymerize to a CR-39-4FMA network copolymer, the preferential component of the LFR. Excellent imaging of the representative LFR is also demonstrated.

INTRODUCTION

A graded index (GRIN) cylindrical medium with a parabolic refractive index distribution expressed as eq. (1)^{1,2} has imaging and light-focusing properties:

$$n(r) = n(0) \left(1 - \frac{1}{2} Ar^2 \right) \quad (1)$$

where $n(0)$ is the refractive index at the center axis, $n(r)$ is the refractive index at a distance r from the center axis, and A is a constant of the refractive index distribution.

The Selfoc rod lens,^{3,4} a glass GRIN-rod lens, is currently manufactured by ion exchange of a cesium-based glass rod and used commercially as an arthroscope,⁵ an imaging device (Selfoc rod lens array) of a new copying machine,⁶ and a connector in fiber communication.⁷

A plastic GRIN-rod lens (designated as a light-focusing plastic rod, LFR) could be prepared by two different processes, namely, by two-step copolymerization⁸⁻¹⁰ (designated diffusion polymerization technique)^{11,12} and by photocopolymerization.¹³⁻¹⁶ The former process is suitable for a rod lens, and a LFR from the latter process can be converted into a GRIN fiber by a heat-drawing process.¹⁷ The two-step copolymerization process of diethylene glycol bis(allyl carbonate) (CR-39) with methacrylic ester of fluorine-containing alcohol (FMA) yields a LFR with excellent convex lens function and with low chromatic aberration.

The change in the chemical composition during the two-step copolymerization of CR-39 with 2,2,3,3-tetrafluoropropyl methacrylate (4FMA) was examined

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to clarify the mode of copolymerization reaction during the fabrication process.

EXPERIMENTAL

Materials

CR-39 (P.P.G. Industries) was distilled at 130–140°C/0.01–0.03 mm Hg. 4FMA (bp 38–40°C/6 mm Hg) was synthesized from methacryloyl chloride and 2,2,3,3-tetrafluoropropanol (Daikin Industry Co.). Benzoyl peroxide (BPO) as initiator was recrystallized from methanol and dried *in vacuo* at room temperature. The reagents for analysis of the allylic group, such as potassium bromide, potassium bromate, potassium iodide, and 0.1*N* aqueous solution of sodium thiosulfate, were commercial by available extra-reagent grade without further purification.

Fabrication of the CR-39-4FMA LFR

CR-39 containing BPO (0.79 wt %) was placed in a polyethylene tube with a 10-mm inner diameter and heated at 90°C for 57 min to yield a prepolymer gel rod (GR).

The GR removed from the polyethylene tube was immersed in 4FMA at T_2 (°C) for t_2 (min) under nitrogen. After draining off 4FMA liquid, the rod was heat treated at 85°C for 20 h under nitrogen to copolymerize the remaining monomer.

The mechanism forming a radial gradient index in the rod was proposed elsewhere¹⁹ on the basis of optical characteristics of the rod. The GR of CR-39 contains a significant amount of CR-39 monomer. In the immersion process, CR-39 diffuses out of the GR, 4FMA diffuses into the GR, and a part of the 4FMA in the GR copolymerizes with the allylic group of the CR-39 unit (Fig. 1). In the heat treatment process, mutual diffusion of CR-39 and 4FMA and copolymerization of 4FMA with the allylic group occur simultaneously. The amount of 4FMA unit fixed by copolymerization increases with distance from the center axis (r); therefore, the refractive index decreases with r due to the higher refractive index of CR-39 homopolymer than that of 4FMA homopolymer.

Measurement of Optical Characteristics of the Rod

In the resulting rod (radius R_p), the index distribution obeys eq. (1) only in the region near the center axis (radius R_c). The index distribution constant A was calculated by the reduction rate γ of the image formed through the rod using eq. (2)^{1,16}:

$$\gamma = \cos(\sqrt{A}Z) - n(0) \sqrt{A}l_1 \sin(\sqrt{A}Z) \quad (2)$$

where Z is the rod length and l_1 is the distance from the object to the end face of the rod. The radius R_c was estimated by using the size of the observed image from our previous paper.^{15,16}

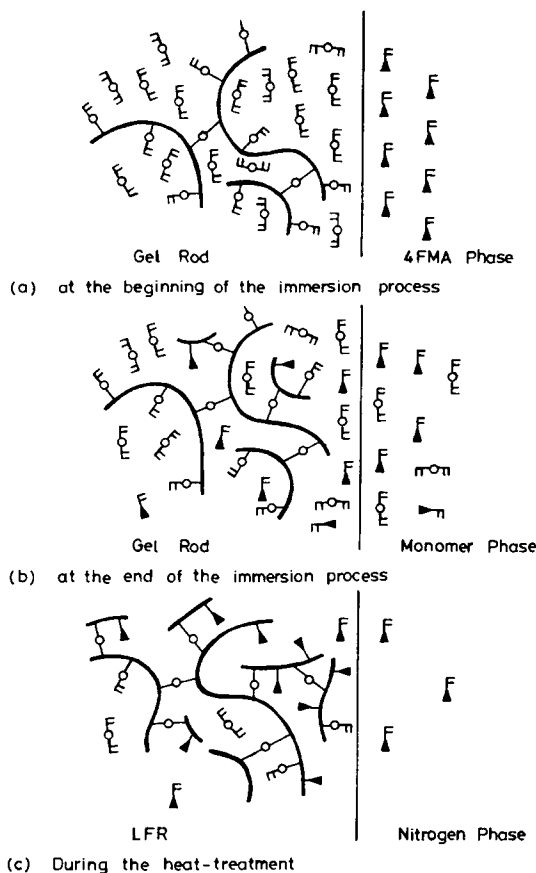


Fig. 1. Schematic representation of the two-step copolymerization process: (---O---) CR-39; $(\text{---}\blacktriangle\text{---})$ 4FMA.

Analysis of Chemical Composition

The GR, the rod after immersion (GRI), and the resulting LFR were separated into the following three fractions by solvent extraction using acetone and methanol: (1) network polymer fraction (W_n), acetone-insoluble part; (2) linear polymer fraction (W_l), acetone-soluble and methanol-insoluble part; (3) remaining monomer fraction (W_m), methanol-soluble part.

The weight fraction of the CR-39 unit in the respective fraction (F_n , F_l , and F_m) was measured by infrared spectrometry (IRS): Absorbances at 792 cm^{-1} due to the carbonate group for the CR-39 unit and 688 cm^{-1} for the 4FMA unit (presumably due to C-F bond) were used. Known mixtures of CR-39 homopolymer and 4FMA homopolymer were employed as standards. The ratio of extinction coefficients for CR-39/4FMA (wt/wt) is 6.3; therefore, a small amount of 4FMA unit is not analyzed quantitatively.

Unsaturation of the CR-39 unit in the respective fraction (U_n , U_l , and U_m) was measured by means of the bromide-bromate method, modifying Simpson's²⁰ procedure as follows: The pulverized sample (0.5–1.0 g) was saponified with $N/2$ alcoholic KOH (10–15 ml) at 20°C for 48 h. After removing the potassium salt by filtration, the solution containing allyl alcohol (2–3 g) was acidified with

acetic acid and $N/2$ potassium bromide–bromate solution was added dropwise with agitation until a yellow color was obtained. After adding an excess (1 ml) of the bromide–bromate solution, 5 ml aqueous 15 wt % KI solution and 100 ml deionized water were added, and excess iodine was titrated with $N/10$ thiosulfate with starch indicator. Even if 4FMA should coexist with CR-39, only the allylic group was determined by this procedure, since the resulting potassium methacrylate was removed by filtration.

RESULTS AND DISCUSSION

Optical Characteristics of LFRs

The GR used was composed of $W_n = 23.6$ wt %, $W_l = 5.6$ wt %, and $W_m = 70.8$ wt %. The LFRs were prepared at $T_2 = 30, 50,$ and 60°C and at $t_2 = 60$ and 120 min; their optical properties are shown in Table I.

Double imaging in IA and IB indicates that in the immersion process at 60°C , the relative copolymerization rate of 4FMA with the allylic group was much faster than the diffusion rate of 4FMA; therefore, the amount of 4FMA at the center axis was too small. On the other hand, immersion at lower temperature, such as 30°C , was suitable. The relations between the preparation conditions and the optical properties of the LFRs are described in detail elsewhere.¹⁹

Representative rod lenses without image distortion were fabricated by removing the periphery region of LFR-IIIB using a centerless grinder. Figure 2 shows excellent imaging properties for this rod lens with a 3.44-mm diameter and a 22.10-mm length, where an image of the test chart was directly formed on a photographic plane (lateral magnification $\times 20$). Here, the figure on the chart $\times 0.024$ represents the line interval (numbers of lines/mm).

Changes in Chemical Compositions in the Preparation Process

The chemical compositions of the LFRs shown in Table II indicate that the preferential component (>85 wt %) in the LFR is the CR-39–4FMA network copolymer; the amount of the remaining monomer (CR-39 + 4FMA) is about 10 wt %, and the amount of the linear polymer is less than 1%. The values of F_l and U_l could not be measured because a sufficient amount of the linear polymer

TABLE I
Optical Properties of LFRs

Code	Immersion condition		$A, 10^{-3} \text{ mm}^{-2}$	R_c/R_p	Imaging property
	$T_2, ^\circ\text{C}$	$t_2, \text{ min}$			
IA	60	60	1.49	0.17	double image ^a
IB		120	1.20	0.11	double image ^a
IIA	50	60	2.68	0.20	good
IIB		120	3.73	0.30	good
IIIA	30	60	3.30	0.46	excellent
IIIB		120	4.14	0.30	excellent

^a Two images are formed on different image planes with different reduction rates (see Ref. 19).

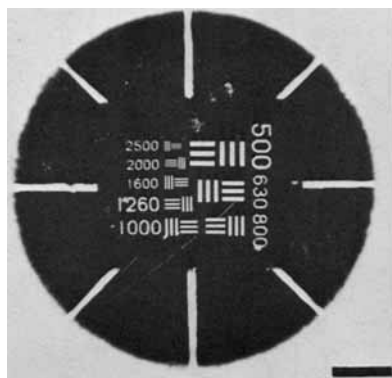


Fig. 2. Image of the test chart formed directly on a photographic plane through CR-39-4FMA LFR of 3.44-mm diameter and 22.10-mm length. Bar represents 10 mm. Number of lines/mm = the figure $\times 0.024$.

for analysis was not obtained. Assuming $F_l = 100$ wt % and $U_l = 50$ mol %, the weight fraction of CR-39 in the LFR (F_0') and the unsaturation of the CR-39 unit in the LFR (U_0') were calculated from the data of the corresponding fractions. The overall weight fraction of CR-39 (F_0) and the overall unsaturation of CR-39 unit (U_0) measured from the pulverized LFR (without fractionation) agree with the respective calculated F_0' and U_0' values (Table II). These results indicate validity of the analysis procedures.

For the rods after immersion, the values of W_n , F_n , W_l , and F_l were measured along with the weight increment. Here, F_l was found to be approximately 100% (the fraction of the linear polymer \approx CR-39 homopolymer). If the weight reduction in the heat treatment is assumed to be exclusively the evaporation loss in 4FMA and not in CR-39, the material balance in the preparation process can be calculated since the amount of CR-39 in the rod after the immersion process (GRI) is equal to that in the corresponding LFR. The calculated results are shown in Figures 2-5, where the subscripts a and b in the sample code refer to the GRI under the condition of $t_2 = 30$ and 60 min, respectively.

When immersed at 60°C, the network fractions in the rods after immersion

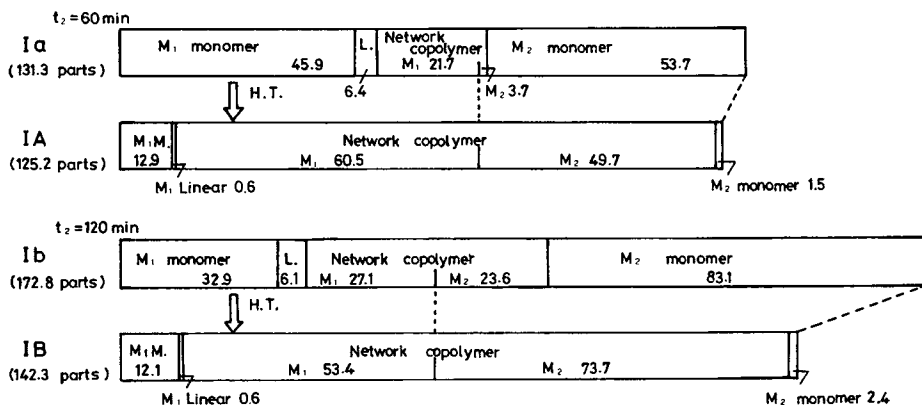


Fig. 3. Material balance (based on 100 parts GR) in the preparation of the CR-39-4FMA LFR at $T_2 = 60^\circ\text{C}$. Sample code is the same as in Table II. Subscripts a and b refer to the rod after immersion.

TABLE II
 Chemical Composition of LFRs^a

Code	Overall				Remaining Monomer			Linear polymer		Network polymer		Weight increment $\Delta W, \%^d$
	3 $F_0, \text{wt } \%$	Observed ^b $U_0, \text{mol } \%$	$F'_0, \text{wt } \%$	Calculated ^c $U'_0, \text{mol } \%$	$W_m, \text{wt } \%$	$F_m, \text{wt } \%$	$U_m, \text{mol } \%$	$W_l, \text{wt } \%$	$U_l, \text{mol } \%$	$W_n, \text{wt } \%$	$U_n, \text{mol } \%$	
Heat-treated GR	100.00	41.92	100.00	38.00	20.50	100.00	87.58	0.98		78.52	100.00	24.90
IA	57.90	35.69	59.07	32.59	11.49	89.43	86.12	0.44		88.07	54.91	21.05
IB	45.49	34.59	46.36	35.40	10.19	83.43	99.64	0.43		89.38	42.02	20.69
F IIA	65.58	33.99	64.11	31.64	11.73	100.00	82.18	0.29		87.98	59.21	20.15
R IIB	54.40	36.91	51.70	32.28	10.81	91.25	82.26	0.24		88.95	46.76	20.33
IIIA	67.77	37.65	67.56	35.15	13.70	100.00	83.04	0.96		85.34	61.99	22.48
IIIB	58.00	36.33	58.82	33.99	11.53	100.00	77.78	0.46		88.01	53.21	23.05

^a W = Amount of corresponding fraction (wt %); F and F' = amount of CR-39 in the corresponding fraction (wt %); U and U' = unsaturation of CR-39 in the corresponding fraction (mol %).

^b Pulverized LFR was used without fractional solvent extraction.

^c Calculated from the data of the corresponding fractions, assuming $F_l = 100 \text{ wt } \%$ and $U_l = 50 \text{ mol } \%$.

^d Based on 100 parts GR.

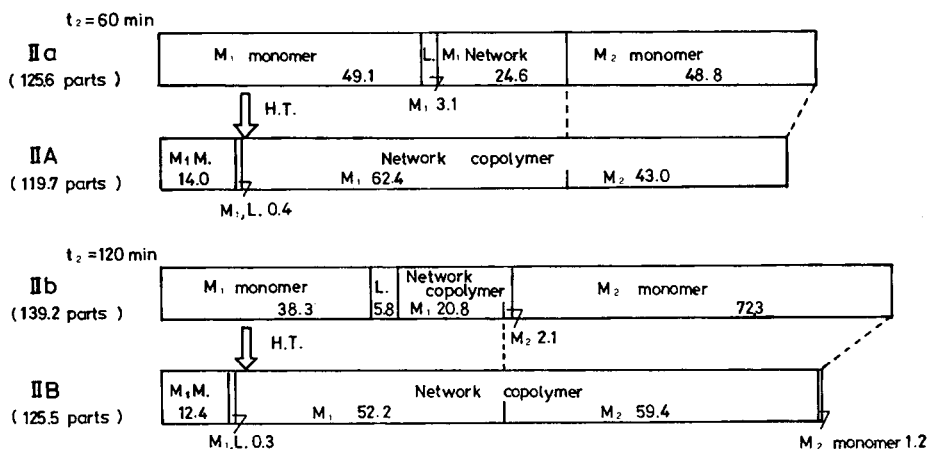


Fig. 4. Material balance (based on 100 parts GR) in the preparation of the CR-39-4FMA LFR at $T_2 = 50^\circ\text{C}$. Sample code is the same as in Table II. Subscripts a and b refer to the rod after immersion.

were CR-39-4FMA copolymers. In the heat treatment, most of the CR-39 was copolymerized with 4FMA to the network copolymer.

In IIa ($T_2 = 50^\circ\text{C}$, $t_2 = 60$ min), the presence of the 4FMA component in the network polymer of the GRI was confirmed by IRS, but its amount was negligible. Increase in immersion time to 120 min (IIb) yielded the network copolymer with a fair amount of 4FMA component. On the other hand, in the case of lower immersion temperature such as $T_2 = 30^\circ\text{C}$, 4FMA component in the network polymer of the GRI was confirmed, but was negligible even when $t_2 = 120$ min. Considering the low extinction coefficient of the C-F bond at 688 cm^{-1} , the network copolymer in the GRI under mild conditions does not contain an appreciable amount of 4FMA component.

Weight balance of monomers in the immersion process were compiled in Figure 6. The amount of 4FMA diffused in the GR or of CR-39 diffused out of the GR

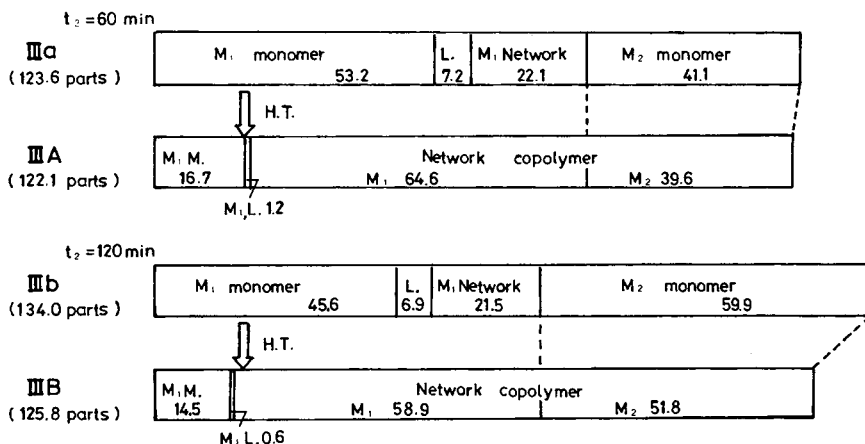


Fig. 5. Material balance (based on 100 parts GR) in the preparation of the CR-39-4FMA LFR at $T_2 = 30^\circ\text{C}$. Sample code is the same as in Table II. Subscripts a and b refer to the rod after immersion.

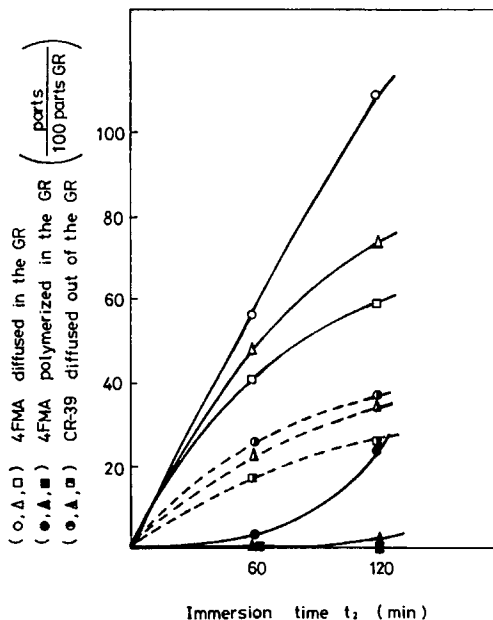


Fig. 6. Weight balance of monomers in the immersion process of CR-39-4FMA system. T_2 ($^{\circ}\text{C}$): (O, ●, ○) 60; (Δ, ▲, △) 50; (□, ■, □) 30.

increased with T_2 and t_2 , but the increment of the respective curve decreased with t_2 presumably due to approach toward the equilibrium state. On the other hand, the amount of 4FMA copolymerized in the GR increased exponentially with t_2 , especially at $T_2 = 60^{\circ}\text{C}$, because the copolymerization rate depends on the product of the CR-39 and 4FMA concentrations in the GR.

Considering the excellent imaging properties of IIIA and IIIB LFRs, the profile of the index distribution is affected by the variation in the component gradient during the heat treatment rather than the immersion process. In addition, the copolymerization of 4FMA with the allylic group in the immersion process, to a significant extent, is not a requisite for fabrication of an excellent rod lens.

CONCLUSIONS

Variations in the weight balance of each component during the preparation process were examined, and the mode of copolymerization was indicated in line with the mode proposed¹⁹ on the basis of optical characteristics of the LFRs. In the immersion process, copolymerization of 4FMA with the allylic group in the gel rod occurs to some extent, depending on T_2 and t_2 . At the end of the process, the rod contains a significant amount of 4FMA and monomeric CR-39. In the heat treatment process, the remaining monomers were copolymerized in the gel rod to a CR-39-4FMA network copolymer which is the preferential component of the LFR. The profile of the index distribution is affected by the variation in the component gradient during the heat treatment rather than in the immersion process.

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