Preparation and Characterization of Light-Focusing Plastic Rod by Swollen-Gel Polymerization

JUI-HSIANG LIU, HUNG-TSAI LIU

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China

Received 31 May 1996; accepted 25 September 1996

ABSTRACT: A new method for preparing light-focusing plastic rod with gradient refractive index (GRIN) profile was fabricated by using the swollen-gel polymerization technique. Monomer pair systems of methyl methacrylate (MMA) with reactive benzyl methacrylate and unreactive bromonaphthalene, benzyl phenyl acetate, benzyl salicylate, triphenyl phosphate, and dibromobenzene were investigated. It was found that refractive index difference and numeric aperture (NA) values of MMA with an unreactive agent are larger than those of a reactive agent system, and a high NA value of 0.336 in a system of MMA/BN = 2/1 was obtained. A distortion-free image can be observed through GRIN rods fabricated by using the swollen-gel polymerization method. Optical characteristics of the GRIN rod were also investigated. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 849–854, 1997

Key words: light-focusing plastic rod; gradient refractive index; optical rod; swollen-gel polymerization; rod lens

INTRODUCTION

The light-focusing plastic rod lens is a cylindrical lens with a parabolic refractive index distribution that is highest on its optical axis and decreases toward the periphery as the square of the radical distance from the optical axis. The refractive index at any distance r from the optical axis is given by the following equation[1,2]:

$$n(r) = n_0[1 - 1/2(Ar^2)] \tag{1}$$

where $n(r)$ is the refractive index at any distance r, n_0 is the refractive index on the optical axis, A is the quadratic gradient constant, and r is the radial distance from the optical axis. A light-focusing plastic rod with a parabolic refractive index distribution is also called a gradient refractive index (GRIN) rod.

Owing to the GRIN distribution in the rod, it has imaging and light-focusing properties, and can be used in copy machines, facsimile lens arrays, and image transmission systems,[3] etc. GRIN polymer optical fibers with a large bandwidth of 2 GHz km and a low optical loss of 56 dB km^{-1} at 688 nm were fabricated,[4] and can be used in communication systems.[5]

Transparent polymers used as GRIN materials have the advantages of excellent mechanical properties, good flexibility, easy processibility, and low cost over quartz glass. Hence, the development of GRIN polymer has grown rapidly in recent years. Several methods have been used to prepare GRIN polymer optical devices, namely, two-step copolymerization,[6–9] photopolymerization,[10,11] chemical copolymerization,[12] suspension polymerization,[13] and interfacial-gel copolymerization.[14]

Like those described in the literature,[14] copolymerization that took place in the interfacial-gel phase is faster than in the monomer mixture solution; thereby, GRIN copolymer is gradually formed in the direction from the periphery to the center of the rod. Although GRIN rod can be pre-

Correspondence to: J.-H. Liu.

pared monolithically by interfacial-gel copolymerization, however, our study and Yang and colleagues' reports[15] show that with this method it is easy to form voids and bubbles resulting from the volume contraction of the GRIN polymer rod. During copolymerization, the monomer solution is not refilled into the polymer tube so a void space caused by the serious shrinkage sometimes tunnels through the polymer rod.

In connection with the studies on the preparation of GRIN rod fabricated in our previous paper,[16] we reported a new method for preparing GRIN rod by using the swollen-gel polymerization technique fabricated in this investigation. With this technique, a GRIN profile can be formed by the swollen gel extending from the peripheral wall of the original plastic tube, and the GRIN rod with no voids and bubbles can be fabricated easily. A distortion-free image can be observed through GRIN rods fabricated by the swollen-gel polymerization method. We studied the effects of reaction temperature, molar ratio of composition, and swollen conditions on the formation of GRIN profile and refractive index difference (Δn) of the rods, and also investigated the image transmission of the GRIN rods.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (99%, from Tokyo Kasei Organic Chemicals [TCI], Tokyo, Japan) was used as a lower refractive index monomer M_1. For M_2, with a higher refractive index (n), we used two different systems: one was the reactive benzyl methacrylate (BzMA, 98%; TCI), and the other was the unreactive agent chosen from bromonaphthalene (BN, 98%; Ferak Chemicals, Germany), benzyl phenyl acetate (BPAc, 99%; TCI), benzyl salicylate (BSA, 99%; TCI), triphenyl phosphate (TPP, 98%; Jassen Chemicals, Belgium), and dibromobenzene (DBB, 99%; TCI). Benzoyl peroxide was used as the initiator. To prevent polymerization from occurring during the swelling period, all commercial materials were used without further purification. Reagent ratios used in this investigation are all weight percentages.

Preparation of GRIN Polymer Rod

Figure 1 shows the diagram of the preparation procedure for the GRIN rod fabricated in this in-

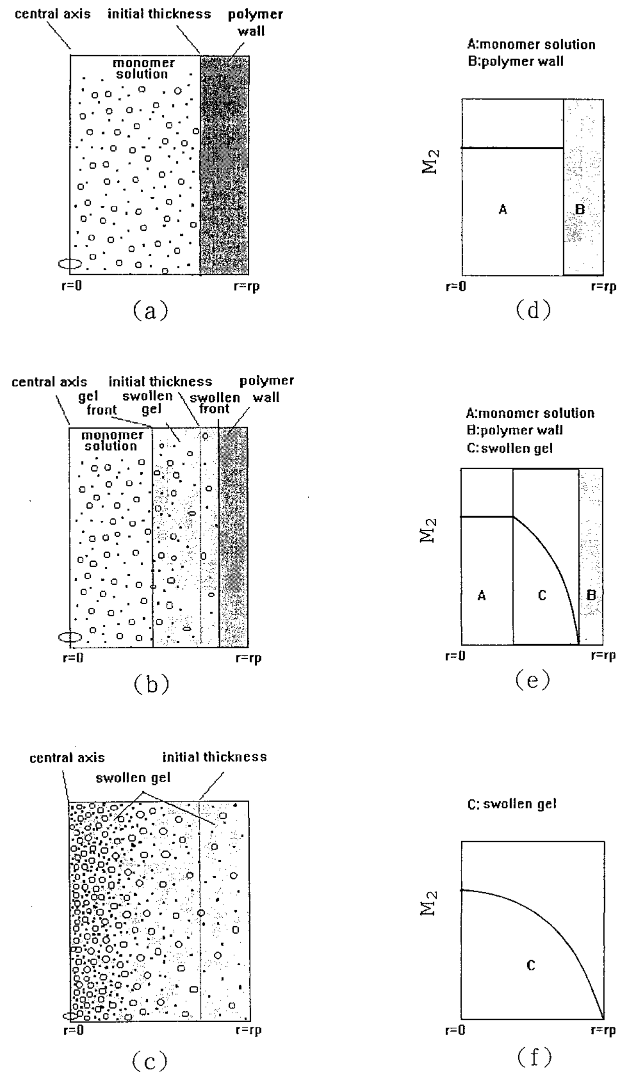


Figure 1 Preparation procedure of GRIN rod using swollen-gel polymerization. (●): M_1, (○): M_2.

vestigation. The monomer mixture (M_1, M_2, and initiator) was poured into a poly(methyl methacrylate) (PMMA) tube. The inner and outer diameters of the tube are 10 and 15 mm, respectively. The tube with monomer mixture was then heated at a lower temperature (T_1) for t_1 hours. During the initial stage, the monomer mixture was absorbed into the inner surface of the plastic tube, and a gel-phase front was formed between the monomer solution and the polymer wall.

Since the solubility parameter of the monomer mixture used in this investigation is near that of polymer, the polymer tube can be easily swollen by the monomer solution. With the monomer solution continuously penetrating into the polymer wall during the swelling period, the swollen gel

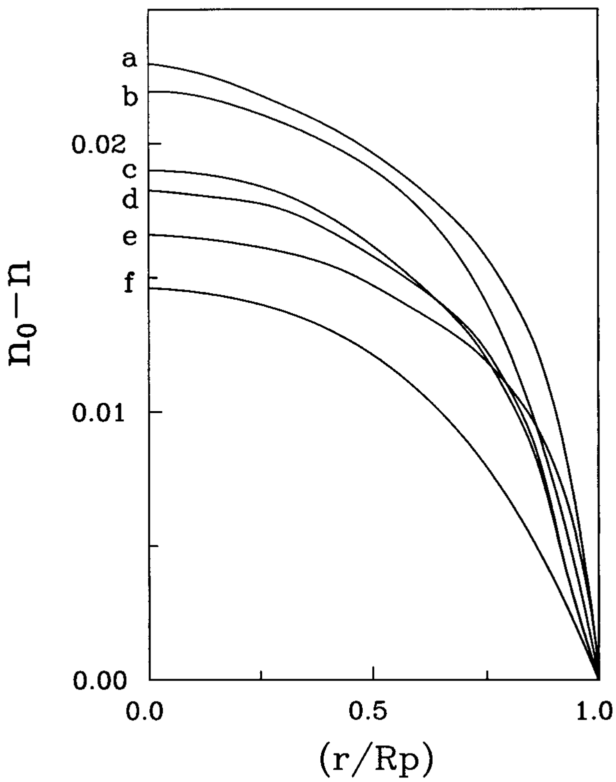


Figure 2 Refractive index profiles of GRIN rods (MMA/M_2 = 4/1). M_2 in curves a, b, c, d, e, and f are BN, BSA, BPAc, TPP, DBB, and BzMA, respectively.

was getting thicker and the polymer wall was getting thinner. Finally, all the mixture in the tube was completely changed into a gel state.

After completion of the swelling process at the lower temperature T_1, the monomer distribution was then fixed by a further polymerization of monomer mixture at a higher temperature, T_2. The monomer mixture and initiator were fully diluted by the swollen gel during the swelling process, and the gel was changed into a rubber state[17] and had less shrinkage than in the liquid monomer solution. Hence, a bubble-free GRIN polymer optical rod was obtained. The refractive index profile of the prepared GRIN rod was measured using a York P102 profile analyzer. The refractive index of the matching oil used in the system is 1.458.

Table I Optical Characteristics of GRIN Rods

Agent	MMA/Agent	No.[a]	Δn	NA	$2\theta_{max}$
BN	4/1	a	0.023	0.264	30.6
	3/1		0.028	0.291	33.9
	2/1		0.037	0.336	39.2
BPAc	4/1	d	0.018	0.235	27.2
	3/1		0.022	0.258	29.9
	2/1		0.026	0.281	32.6
BSA	4/1	b	0.022	0.258	29.9
	3/1		0.026	0.281	32.6
	2/1		0.034	0.322	37.5
TPP	4/1	c	0.019	0.239	27.7
DBB	4/1	e	0.017	0.224	25.9
BzMA	5/1	f	0.012	0.190	21.9
	4/1		0.014	0.201	23.5
	3/1		0.015	0.213	24.6

Swollen at 40°C for 30 h and then heated at 80°C for 24 h.
[a] Curve number in Figure 2.

RESULTS AND DISCUSSION

As shown in Figure 2, monomer concentration depends on the radial direction resulting from the penetration of monomer mixture changed from the periphery to the center of the gel rod. The concentration of higher refractive index material M_2 is decreased from the center to the periphery of the gel rod, and resulted in a GRIN distribution.

After completion of the swelling process, as shown in Figure 1(f), the monomer concentration of M_2 is distributed in gel phase. The distribution was confirmed by using a refractive index analyzer. Although the penetration of the monomer mixture almost reached the brink of the tube wall, the tube structure was maintained with no structural deformity.

Optical characteristics of GRIN rods prepared by swollen-gel polymerization with various materials and molar ratios are listed in Table I. Where Δn is the refractive index difference between the center and the periphery of the rod, NA is the numeric aperture, and θ_{max} is the maxium acceptance angle, all can be calculated from the following equation:

Table II Refractive Index of Agents

Agents	MMA	BzMA	BN	BSA	BPAc	TPP	DBB
n	1.490	1.586	1.660	1.580	1.555	1.550	1.574

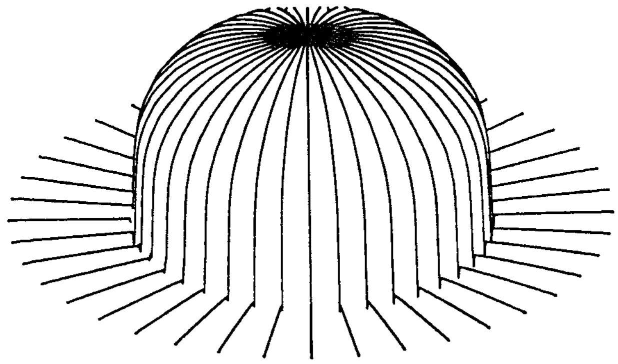


Figure 3 3-D refractive index profile of GRIN rod (MMA/BPAc = 4/1).

$$NA = \sin \theta_{max} = (2 \times \Delta n \times n_0)^{0.5} \quad (1)$$

Here n_0 is the refractive index at the center of the rod.

Table I shows that Δn, NA, and θ_{max} all increased with increased amounts of the M_2 agent, and that the MMA/BN system has a higher Δn owing to the higher refractive index of BN ($n = 1.66$). (See Table II for complete list of refractive indices.) Compared with the MMA/reactive agent system (MMA/BzMA), MMA/unreactive agent systems (MMA/BN, MMA/BPAc, MMA/BSA, MMA/TPP, and MMA/DBB) seem to have higher Δn and NA values. Even when the amount of BzMA is increased to MMA/BzMA = 3/1, the Δn and NA of MMA/BzMA rod are still less than those of MMA/unreactive agent in a ratio of 4/1. These results suggest that an unreactive agent dispersed in PMMA matrix seems to have a higher refractive index than that of the copolymer of reactive agent BzMA with MMA.

Figure 2 shows GRIN profiles of the rods prepared by the swollen-gel polymerization method using MMA/BN, MMA/BSA, MMA/TPP, MMA/BPAc, MMA/DBB, and MMA/BzMA material pairs in the ratio of 4/1, respectively. As seen in Figure 2, Δn of MMA/BN, MMA/BSA, MMA/TPP, MMA/BPAc, MMA/DBB, and MMA/BzMA rods decrease in that order. As we know, high NA value or high acceptable angle (θ_{max}) will bring about a high brightness, and the high brightness is a necessary factor for the GRIN lens to achieve high-speed scanning or make the machine com-

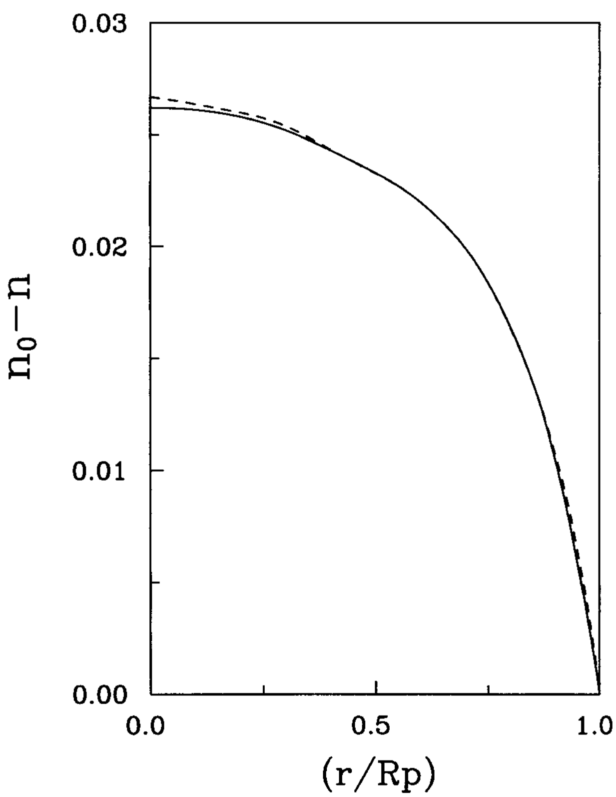


Figure 4 Stability of the index distribution of MMA/BPAc = 4/1 rod. (———): original index profile; (– – –): after heating at 100°C for 48 h.

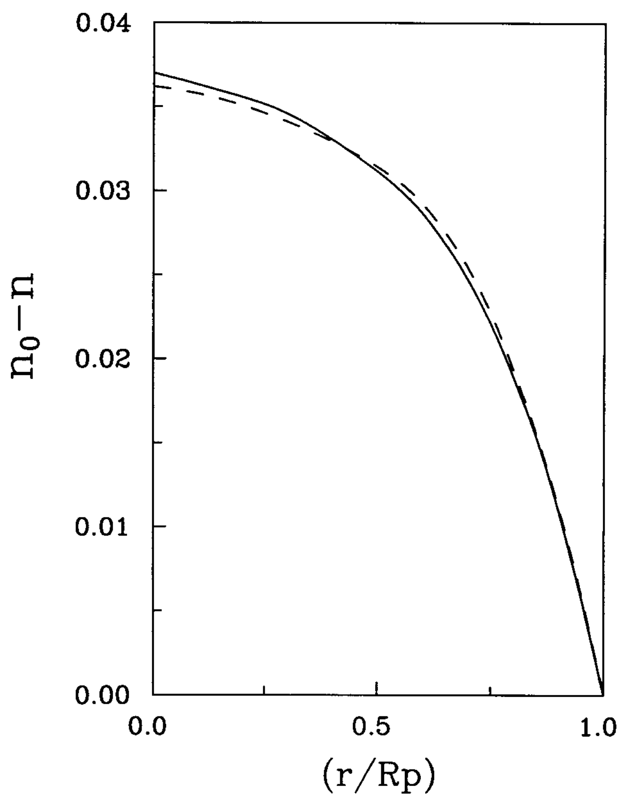
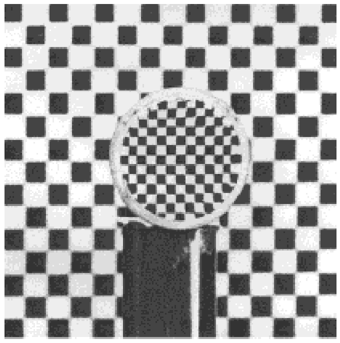
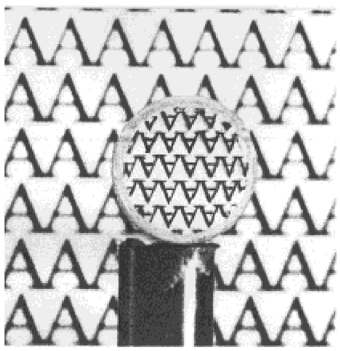


Figure 5 Storage stability of the index distribution of MMA/BN = 2/1 rod. (———): original index profile; (– – –): after heating at room temperature for 100 days.



(a)



(b)

Figure 6 Image observed through the MMA/BPAc = 4/1 rod with 15 mm diameter and 145 mm length. (a) Real image of a 7 × 7-mm^2 checker pattern; distance between the object and the end of rod is 200 mm. (b) Real image of letters A with 16 mm height and 15 mm width. The distance between the object and the end of rod is 250 mm.

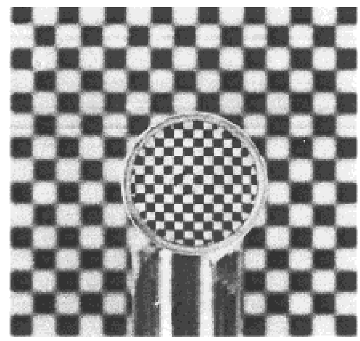
pact when using GRIN rods in image-transmission systems.

As seen in Table I a GRIN rod with the high NA of 0.336 is obtained from MMA/BN = 2/1; however at MMA/BzMA = 2/1 an obvious phase separation occurred in the rod, resulting in obscurity. These results suggest that unreactive agents such as BN, BPAc, BSA, etc., can be well dissolved in PMMA matrix, and that a large amount of BzMA monomer in the system will cause the homopolymerization of BzMA and result in phase separation.

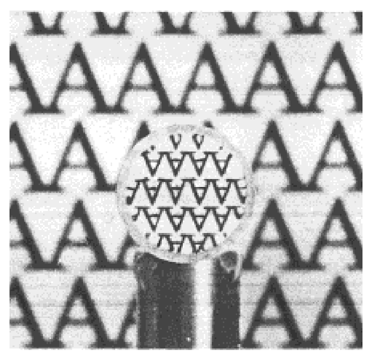
A two-dimensional refractive index profile of rods was estimated; the results, summarized in Figure 2, show that the refractive index profiles are almost quadratic from the center axis to the periphery. Figure 3 shows the three-dimensional refractive index profile of a GRIN rod. The results suggest that a good symmetric GRIN rod can be fabricated by using swollen-gel polymerization.

Figure 4 shows the stability of the index distribution of the fabricated rod (MMA/BPAc = 2/1) after reheating at 100°C for 48 h. The storage stability of the refractive index profile of the MMA/BN = 2/1 rod was also evaluated. The GRIN rod was stored at room temperature for 100 days. As shown in Figure 5, no remarkable deviations have been considered. The results suggest that the unreactive agent distributed in GRIN rod is very stable.

Figure 6 shows the real images of a checkered pattern of 7 mm^2 squares and of letters A with 16 mm height and 15 mm width. The images were formed through the rod prepared in an MMA-and-



(a)



(b)

Figure 7 Image observed through the MMA/BzMA = 4/1 rod with 15 mm diameter and 165 mm length. (a) Real image of a 7 × 7-mm^2 checker pattern; distance between the object and the end of rod is 250 mm. (b) Real image of letters A with 16 mm height and 15 mm width. The distance between the object and the end of rod is 300 mm.

unreacted-agent system (MMA/BPAc = 4/1). Here the diameter and length of the rod are 15 mm and 145 mm, respectively. The distance between the checkered pattern and the end face of the GRIN rod is 200 mm, and the distance between letters A and the end face of the GRIN rod is 250 mm.

Figure 7 shows the real images which were formed through the GRIN rod prepared in an MMA-and-reactive-agent system (MMA/BzMA = 4/1). The objects are the same as those in Figure 6 but the diameter and length of the rod are 15 mm and 165 mm, respectively. The distance between the checkered pattern and the end face of the GRIN rod is 250 mm, and the distance between letters A and the end face of the GRIN rod is 300 mm.

As shown in Figures 6 and 7, no image distortion was found. The results suggest that GRIN plastic optical rod can be fabricated by using the swollen-gel polymerization method.

CONCLUSION

A novel method for preparing GRIN plastic rod was fabricated by using the swollen-gel polymerization technique. Systems combining MMA with reactive and unreactive agents were investigated. It was found that Δn and NA values of MMA with an unreactive agent are larger than those of an MMA–reactive agent system, and a high NA value of 0.336 in MMA/BN = 2/1 was obtained. Images with almost no distortion can be observed through the GRIN rods fabricated by using the swollen-gel polymerization method.

REFERENCES

1. F. P. Kapron, *J. Opt. Soc. Am.,* **60,** 1433 (1970).
2. E. G. Rawson, D. R. Herriott, and J. Mckenna, *Appl. Opt.,* **9,** 753 (1970).
3. Y. Koike, "Gradient Index Materials and Components," in *Polymers for Lightwave and Integrated Optics,* L. A. Hormak, Ed., Marcel Dekker, Inc., New York, 1992.
4. Y. Koike, T. Ishigure, A. Horibe, and E. Nihei, *Proc. Second Int. Conf. Plastic Optical Fibers and Applications,* Geneva, 1993, p. 54.
5. J. Wilson and J. F. B. Hawkes, *Optoelectronics: An Introduction,* Prentice-Hall, New Jersey, 1983, pp. 357 and 377.
6. Y. Ohtsuka and Y. Terao, *J. Appl. Polym. Sci.,* **26,** 2907 (1981).
7. N. Yamamoto and K. Iga, *Appl. Opt.,* **19,** 1101 (1980).
8. Y. Ohtsuka and T. Sugaho, *Appl. Opt.,* **22,** 413 (1983).
9. Y. Ohtsuka and T. Senga, *J. Soc. Polym. Sci. Jpn.,* **35,** 721 (1978).
10. Y. Koike, Y. Kimoto, and Y. Ohtsuka, *Appl. Opt.,* **21,** 1057 (1982).
11. Y. Koike, Y. Kimoto, and Y. Ohtsuka, *J. Appl. Polym. Sci.,* **27,** 3253 (1982).
12. Y. Koike, H. Hidaka, and Y. Ohtsuka, *Appl. Opt.,* **24,** 4321 (1985).
13. Y. Koike, Y. Sumi, and Y. Ohtsuka, *Appl. Opt.,* **25,** 3350 (1986).
14. Y. Koike, Y. Takezawa, and Y. Ohtsuka, *Appl. Opt.,* **27,** 486 (1988).
15. S. Y. Yang, B. C. Ho, J. J. Chen, T. W. Tseng, and M. S. Lee, *SPIE,* **2000,** 396 (1993).
16. J. H. Liu and C. D. Chou, *Angew. Makromol. Chem.,* **174,** 1 (1991).
17. G. C. Sarti, C. Gostoli, G. Riccioli, and G. Carbonell, *J. Appl. Polym. Sci.,* **32,** 3627 (1986).