Optical Gradient Materials Produced via Low-Temperature Isothermal Frontal Polymerization

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ABSTRACT: Using a newly developed low-temperature frontal polymerization technique, poly(methyl methacrylate) (PMMA) matrices were prepared with nonuniform distributions of organic nonlinear optical dyes, with potential use as optical limiters. This technique affords lower temperature conditions than have been used before. A PMMA tube was filled with a dye, the initiator *tert*-butyl peroxide, and methyl methacrylate (MMA). Curing at 4°C resulted in a radial gradient of dye. An axial dye gradient was observed when MMA was overlaid and polymerization effected from a dye-doped PMMA seed using tricaprylmethyl ammonium persulfate as the initiator. In both cases, polymerization reactions were observed as a result of isothermal frontal polymerization with the subsequent formation of a nonlinear concentration distribution of the optical dye dopants. Low temperatures are desirable to eliminate thermal and photothermal degradation of temperature-sensitive dyes during the polymerization. The preparation of long polymer rods with organic dye gradients on the scale of several centimeters can also be realized with the use of low-temperature polymerization and the gradients controlled by the concentration of initiator. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 686–691, 2001

Key words: optical limiters; isothermal frontal polymerization; functional gradient materials; interfacial-gel polymerization; gel effect; propagating fronts

INTRODUCTION

Gradient Index Materials

Polymers are gaining popularity as media for solid-state lasers,[1–4] optical limiters[5] as well as fiber optics.[6,7] The use of polymer-based materials in tandem with electronic technology offers a viable option for inexpensive networking materials.[8] Many researchers have successfully explored the coupling of the current electronic technology with novel materials such as gradient ref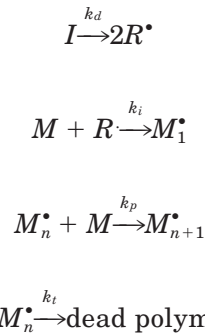ractive index (GRIN) materials based on glass[9,10] and polymers.[11,12] GRIN materials have already found application in fiber optics.[6,7]

There are three types of GRIN media, namely, radial, axial and spherical.[11] Radial GRIN media are characterized by a continuous gradient that varies along the radius of a cylinder. On the other hand, axial GRINs have a compositional gradient that varies along the optical axis. Spherical GRINs constitute the third type of GRIN media and have gradients that vary spherically.

Although glass-based materials have been in use for a fairly long time, polymeric materials are now receiving considerable attention particularly in the area of optoelectronics because plastic optical fiber (POF) materials offer a number of advantages over glass materials viz. good ductility,

$$I \xrightarrow{k_d} 2R^{\bullet}$$

$$M + R^{\bullet} \xrightarrow{k_i} M_1^{\bullet}$$

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}$$

$$2M_n^{\bullet} \xrightarrow{k_t} \text{dead polymer}$$

Scheme 1 A summary of four steps in a free radical polymerization with a thermal initiator.

light weight, ease of splicing, and low manufacturing costs. Thus, POFs offer the combined qualities of glass as well as the low cost of copper cables while precluding disadvantages like brittleness and electromagnetic interference associated with glass and copper, respectively.

Review of Isothermal Frontal Polymerization

The preparation of GRINs for POFs is based on the coupling of autocatalysis and diffusion in an unstirred system. Free radical polymerization reactions can exhibit autocatalysis through the gel effect, also known as the Trommsdorf-Norris (TN) effect.[13,14] Consider such a polymerization reaction (Scheme 1), in which **I** is the initiator, R⁻ denotes free radicals from the thermal decomposition of the initiator and, M^*_n are polymeric macroradicals where $n = 1, 2 \ldots n$. Autocatalysis is realized because of the greater dependence of the termination step on viscosity than the propaga-
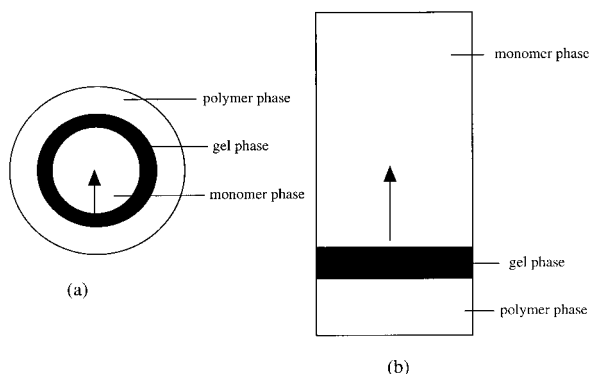

Figure 1 A schematic depiction of interfacial-gel polymerization technique for radial gradients (a) and axial gradients (b). The arrows show the direction of polymerization growth.
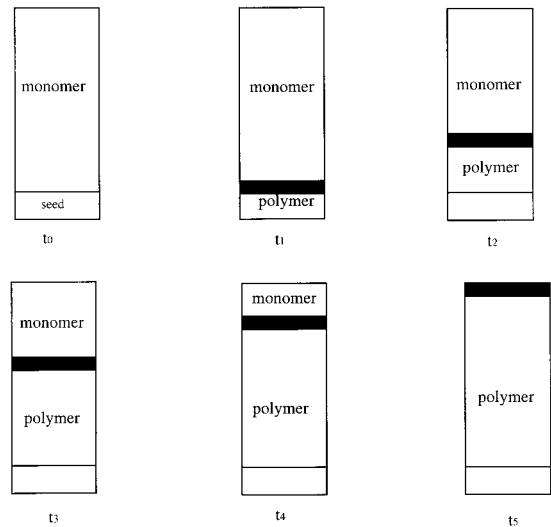

Figure 2 A schematic representation of a "narrow" polymerization reaction zone propagating along the axis of the test tube.

tion step. As the polymerization progresses, there is an increase in viscosity and a decrease in the termination rate, and, thus, an increase in the rate of polymerization.

Koike et al.[15] first reported using the gel effect in 1988 in a process they called "interfacial gel polymerization," and applied it to GRIN fabrication.[11,16,17] Smirnov et al.[18,19] reported a similar process in 1993, calling it "frontal polymerization." We refer to the process as isothermal frontal polymerization (IFP) to distinguish it from thermal frontal polymerization discovered in 1972, in which a localized reaction propagates through the coupling of thermal diffusion and the Arrhenius dependence of the polymerization.[20,21] Spade and Volpert[22–24] successfully modeled IFP.

Initially, the monomer and initiator soak into a polymer seed to form a "gel" (a very viscous solution) (Fig. 1). Once in the gel, the polymerization ensues and progresses at a faster rate than in the liquid phase because of the gel effect. The general basis of isothermal frontal polymerization is summarized in Figure 2, in which a solution of monomer and initiator is overlaid onto a polymer seed at time t_0. After time t_1, the seed serves as the initiation site upon soaking the monomer to give a gel. The formation of the gel leads to the facilitated polymerization, and thus the gel becomes a localized reaction zone. Further polymerization results in the conversion of the gel phase to a polymer phase. The nascent polymer phase

becomes the new seed, and, consequently, the process becomes self-propagating, with the reaction zone converting the liquid-state monomer to a solid-state polymer as it propagates along the test tube, t_2–t_5.

## Preparation of GRINS and Organic Optical Limiters via IFP

The preparation of GRIN materials via IFP was pioneered by Koike.[3,7,11,12,15–17,25–32] Zhang et al.[33] reported a "novel interfacial-gel polymerization" technique for GRIN formation, but it is a variant of the Koike method using bromobenzene as the high-refractive index dopant. The approach is simple: In the monomer/initiator solution, a dopant is dissolved that has a higher refractive index than the polymer. As the interface propagates, the dopant accumulates in the bulk solution. Ultimately, the sample has a gradient of dopant concentration, and thus a gradient in refractive index. Alternatively, the dopant can be present in the seed, and leaches out during front propagation.

Organic Optical Limiters

An optical limiter is a device that strongly attenuates intense optical pulses but allows high transmittance of low-intensity light. Such a device would be very useful for protecting human eyes from intense laser pulses.[34] Perry et al.[35] discussed the types of organic materials that exhibit such nonlinear absorption. They have found that metallophthalocyanine (M-Pc) complexes containing heavy central atoms work well. These dyes are compatible with poly(methyl methacrylate) and dissolve in the monomer.[35]

Miles calculated that the maximum attenuation of a light pulse can be achieved if the absorbing species is distributed as a hyperbolic function of position, as illustrated in Figure 5.[36] Perry et al.[35] demonstrated the value of a gradient by approximating the hyperbolic distribution with slabs containing different dye concentrations at set distances.

Reported techniques produce gradients at 70 °C on the scale of a few millimeters. The limiting factor is the bulk polymerization of the monomer/initiator solution, which can be suppressed with the addition of a polymeric inhibitor.[18] However, we sought another technique that would allow control over the dye distribution on the centimeter scale. Spade and Volpert[22–24] modeled isother-
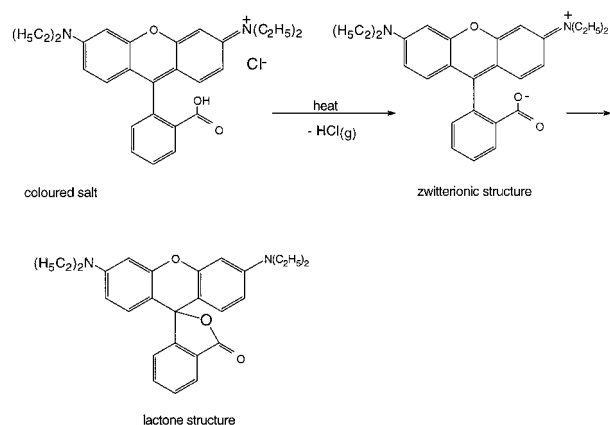
Scheme 2   Thermally induced loss of optical activity of Rhodamine B.

mal frontal polymerization, and found that at higher temperatures the front propagates more rapidly than at lower temperatures but for a shorter period of time until bulk polymerization occurs. Thus, using low temperatures results in slow propagation but for a longer distance.

Tagaya et al.[3] noted doping organic dyes into graded index polymer optical fibers posed some problems. Rhodamine dyes with a carboxylic acid moiety tend to isomerize yielding a colorless inner lactone structure, particularly in nonpolar media and, subjecting these dyes to a high concentration of free radicals often leads to the decomposition of the dyes. They proposed and successfully demonstrated the use of mercaptan compounds to suppress the decomposition of rhodamine dyes during polymerization.

The use of mercaptan compounds presupposes that the formation of the colorless inner lactone is preceded by the electrolytic dissociation of the carboxylic acid, especially in the presence of water.[3] Even in the absence of water, high temperatures can also lead to lactone formation, as shown in Scheme 2.

The thermally induced electrolytic dissociation of the carboxylic acid is thermodynamically favored due to the release of gaseous HCl to give the zwitterionic intermediate. The formation of the lactone is driven by two factors: an increase in aromaticity and the enhanced solubility of the lactone in the low-polar MMA. Yee et al.[4] found that RB-PMMA slabs made via hot-press molding had significantly reduced dye absorption, by a factor of 3–4, in comparison with dried spongy PMMA preforms.

This thermal bleaching mechanism depends on the nature of the anion in the Rhodamine dyes. With chloride as the anion, Higuchi and Muto observed a dramatic thermal bleaching at temperatures between 65 and 83°C, the same temperature range within which POFs are fabricated.[37] On the other hand, bleaching was nominal when chlorate was the anion, which would produce $HClO_4$ upon protonation. Thus, by utilizing low-temperature conditions, the decomposition of the dye is minimized.

EXPERIMENTAL PROCEDURES

Materials

The following materials were used from Aldrich as received: methyl methacrylate (MMA), *tert*-butylperoxide (*t*-BPO), dimethyl sulfoxide (DMSO), naphthalene, aluminum phthalocyanine chloride (APC), Rhodamine B (RB), ammonium persulfate, and Aliquat 336 (tricaprylmethylammonium) chloride. The inhibitor methylhydroquinone (MEHQ) in the monomer was removed using a manufacturer-supplied kit. Tricaprylmethylammonium persulfate (Aliquat persulfate, APSO) was synthesized according to the procedure of Chekanov et al.[39] Plexiglas (PMMA) tubes with an external radius of 0.65 cm and an internal radius of 0.33 cm were purchased from McMaster-Carr Supply Co.

Preparation of PMMA Seeds

Experiments were performed in 1.5 cm (i.d.) test tubes. Dye-free seeds were made by mixing 18 mL of MMA and 2 mL of *t*-BPO. Into each of 20 test tubes, 2 mL of this solution was charged, the tubes capped, and incubated in an oven set at 90°C. The MMA solutions polymerized into translucent PMMA seeds within 2 h. Similarly, seeds doped with APC were made by combining 16 mL of MMA, 2 mL of *t*-BPO and 2 mL of 4.3 m*M* APC dye dissolved in DMSO and curing at 90°C for about 12 h.

Preparation of Radial PMMA-RB and Axial APC-PMMA GRIN Rods

A solution of RB, Aliquat persulfate, naphthalene, and MMA was placed in a Plexiglas tube capped on one end with a rubber septum and incubated at 4°C for 3 days. The resultant RB radial gradient was put in an oven at 70°C for 2 h to complete polymerization.

Axial APC dye gradients were prepared by overlaying dye-doped seeds with a solution of MMA containing Aliquat persulfate as the initiator. Depending on the desired duration and length of the gradient dye, the test tubes were allowed to react at 4°C. The spatial distribution profile of the optical dyes the polymer rods were analyzed with an AlphaImager 2000 Documentation Analysis System.

RESULTS AND DISCUSSION

PMMA-APC Axial Gradients

APC gradients were prepared by making a polymer seed doped with APC over which a dye-free reaction mixture of MMA and an initiator was placed. This process yields dye gradients because the monomer diffuses into the seed while the dye diffuses into the monomer/initiator solution. By varying the incubation temperature and the concentration of the initiator, the rate of the leaching of the dye and the rate of front propagation were carefully controlled to give a gradient of the desired length. The most remarkable aspect was the low incubation temperatures required. Under room temperature conditions, the growth of the polymer rod far exceeded the diffusion of the dye, leading to a comparatively short dye gradient and opaque polymer rods. Lower temperatures, on the other hand, resulted in fronts with slow propagation speed relative to the diffusion of the optical dye and, as a result, the distribution of the dye was almost homogeneous. Undesirable weak dye gradients were thus produced. However, once the optimum initiator concentration and incubation temperatures were established, transparent polymer rods were produced, as shown in Figure 3. Dye concentration profiles of APC gradients produced at different initiator concentrations are shown in Figure 4. They can be fit to a fourth-order polynomial.

Rhodamine Radial Gradients

Curing the sample at 4°C produced a radial gradient of the dye, as shown in Figure 5. The spatial color distribution can be fit to a fourth-order polynomial. It is apparent that using low-temperature polymerization could not only reduce thermal
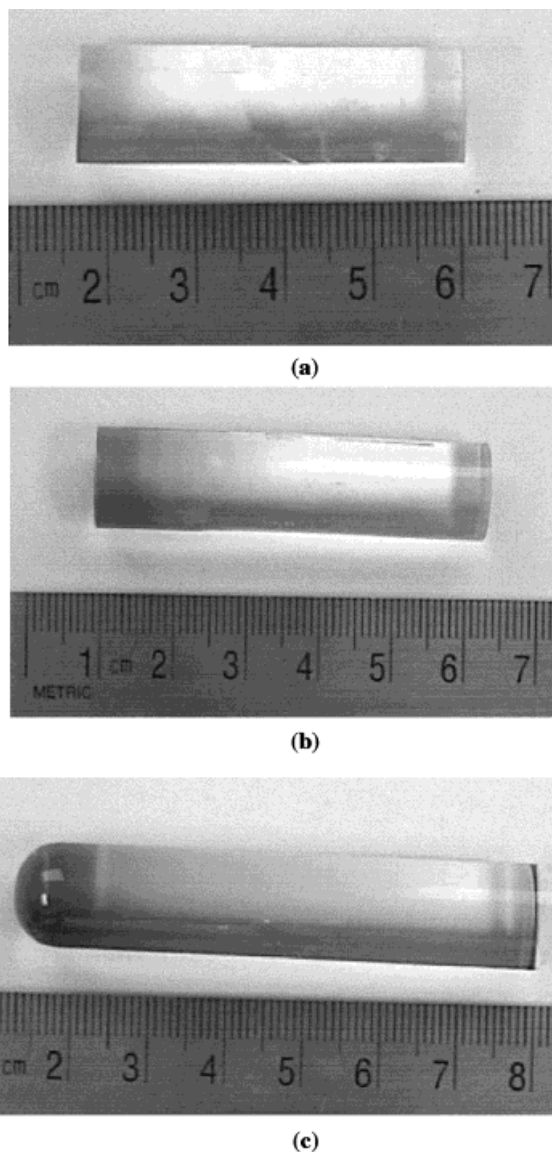
(a)

(b)

(c)

Figure 3 PMMA-APC optical limiter axial gradient rods prepared via the low-temperature (4°C) interfacial-gel polymerization approach. The rods show the dependence of the length of the dye gradient on the concentration of Aliquat persulfate: the concentration used for (a), (b), and (c) are $2.0 \times 10^{-4}\,M$, $1.0 \times 10^{-4}\,M$, and $5.0 \times 10^{-5}\,M$, respectively.

bleaching but could be another alternative to photoinitiation,[38] shown to cause photothermal bleaching of the dyes,[1,2] regardless of the anion.

CONCLUSION

A low-temperature isothermal frontal polymerization technique was developed to prevent ther-
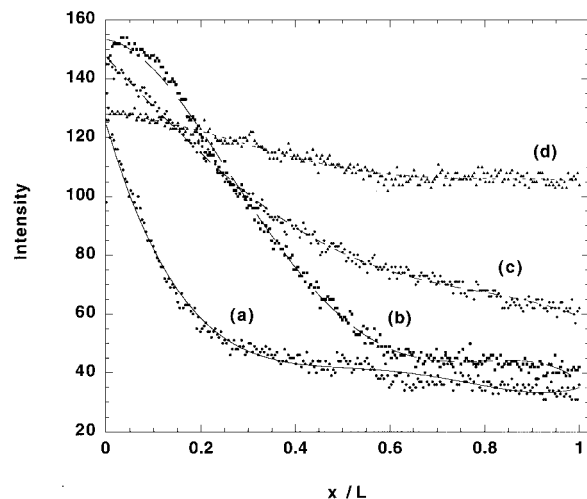

Figure 4 Dye distribution of the PMMA-APC gradient optical limiters. The concentration used for (a), (b), (c), and (d) are $2.0 \times 10^{-4}\,M$, $1.0 \times 10^{-4}\,M$, 5.0×10^{-5}, and $2.5 \times 10^{-5}\,M$, respectively.

mal degradation of organic dyes during the preparation gradient materials. The preclusion of bulk polymerization at low temperatures also meant that long axial polymer rods with potential uses in optical devices could be produced. High-temperature techniques would normally suffice for millimeter-scale axial gradients but, for longer axial gradients, precluding bulk polymerization is always problematic at high temperatures. By in-
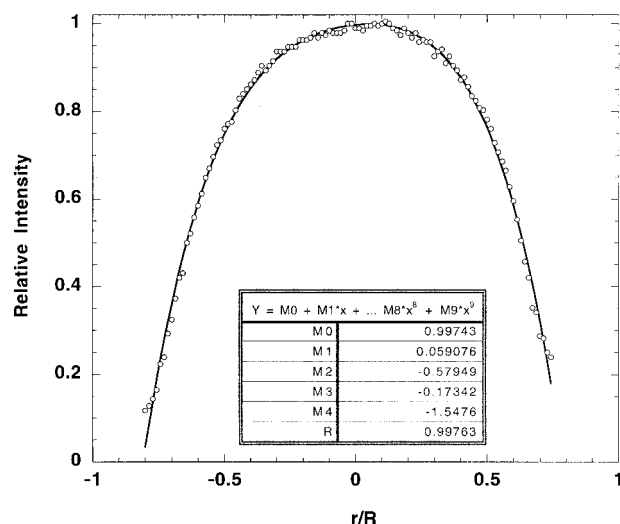

Figure 5 A radial profile of RB6 laser dye prepared via the low-temperature interfacial-gel polymerization (solid circles), and the solid line is a fourth-order polynomial fit. $R = 0.65$ cm.

troducing low-temperature conditions, it was demonstrated that plastic-based optical materials can be produced under less stringent conditions than the procedures used before now, notably, the use of high temperatures in tandem with free-radical inhibitors. Moreover, the dye distribution can be controlled by varying the initiator concentration.

REFERENCES

1. Gromov, D. A., et al. J Opt Soc Am 1985, B2, 1028.
2. Dyumaev, K. M., et al. J Opt Soc Am 1992, B9, 143.
3. Tagaya, A.; Teramoto, S.; Nihei, E.; Sasaki, K.; Koike, Y. Appl Opt 1997, 36, 572.
4. Yee, K. C.; Tou, T. Y.; Ng, S. W. Appl Optics 1998, 37, 6381.
5. McLean, D. G. Soc Photo-Opt Instrum Eng 1997, 3146, 72.
6. Tomlinson, W. J. Appl Opt 1980, 19, 1127.
7. Ishigure, T.; Nihei, E.; Koike, Y. Appl Opt 1994, 33, 4261.
8. Ai, J.; Li, Y. Appl Opt 1999, 38, 325.
9. Moore, D. T. Appl Opt 1980, 19, 1035.
10. Samuels, J. E.; Moore, D. T. Appl Opt 1990, 29, 4042.
11. Koike, Y. In Polymers for Lightwave and Integrated Optics; Hornak, L. A., Ed.; Marcel Dekker: New York, 1992, p. 71.
12. Nihei, E.; Ishigure, T.; Koike, Y. Appl Opt 1996, 35, 7085.
13. Trommsdorff, E.; Köhle, H.; Lagally, P. Makromol Chem 1948, 1, 169.
14. Norrish, R. G. W.; Smith, R. R. Nature 1942, 150, 336.
15. Koike, Y.; Takezawa, Y.; Ohtsuka, Y. Appl Opt 1988, 27, 486.
16. Koike, Y.; Nihei, E.; Tanio, N.; Ohtsuka, Y. Appl Opt 1990, 29, 2686.
17. Koike, Y. Polymer 1991, 32, 1737.
18. Smirnov, B. R.; Lusinov, I. A.; Sidorenko, A. A.; Stegno, E. V.; Ivanov, V. V. Vysokomol Soedin, Ser B 1993, 35, 161.
19. Ivanov, V. V.; Stegno, E. V.; Pushchaeva, L. M. Chem Phys Rep 1997, 16, 947.
20. Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. Dokl Akad Nauk SSSR 1972, 204, 1180.
21. Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. J Chem Soc Faraday Trans 1996, 92, 2825.
22. Spade, C. A.; Volpert, V. A. Math Comp Modelling 1999, 30, 67.
23. Spade, C. A.; Volpert, V. A. Chem Eng Sci 2000, 55, 641.
24. Spade, C. A.; Volpert, V. A. Macromol Theory Simul 2000, 9, 26.
25. Wu, S. P.; Nihei, E.; Koike, Y. Polym J 1995, 27, 21.
26. Koike, Y.; Hatanaka, H.; Otsuka, Y. Appl Opt 1984, 23, 1779.
27. Koike, Y.; Hidaka, H.; Ohtsuka, Y. Appl Opt 1985, 24, 4321.
28. Koike, Y.; Nihei, E. U.S. Pat. 1993.
29. Koike, Y.; Asakawa, A.; Wu, S. P.; Nihei, E. Appl Opt 1995, 34, 4669.
30. Ohtsuka, Y.; Koike, Y. Appl Opt 1984, 23, 1774.
31. Ohtsuka, Y.; Koike, Y. Appl Opt 1985, 24, 4316.
32. Sasaki, K.; Koike, Y. U.S. Pat. 1995.
33. Zhang, Q.; Wang, P.; Zhai, Y. Macromolecules 1997, 30, 7874.
34. Crane, R.; Lewis, K.; Stryland, E.V.; Koshnevisan, M., Eds. Materials for Optical Limiting; Materials Research Society: Pittsburgh, PA, 1995, vol. 374.
35. Perry, J. W., et al. Science 1996, 273, 1533.
36. Miles, P. Appl Opt 1994, 33, 6965.
37. Higuchi, F.; Muto, J. Phys Lett 1981, 81A, 95.
38. Ohtsuka, Y.; Terao, Y. J Appl Polym Sci 1981, 26, 2907.
39. Chekanov, Y.; Pojman, J. A.; Rasmussen, J. K. Polym Prepr (Am Chem Soc Div Polym Chem) 1998, 39, 465.