**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# High Refractive Index Polymers for Optical Applications

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**To cite this Article** Beecroft, L. L. and Ober, C. K.(1997) 'High Refractive Index Polymers for Optical Applications', Journal of Macromolecular Science, Part A, 34: 4, 573 — 586
**To link to this Article: DOI:** 10.1080/10601329708014985
**URL:** http://dx.doi.org/10.1080/10601329708014985

J.M.S.—PURE APPL. CHEM., A34(4), pp. 573–586 (1997)

# HIGH REFRACTIVE INDEX POLYMERS FOR OPTICAL APPLICATIONS

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## ABSTRACT

High refractive index (RI) materials are extremely important in many optical applications. Polymers traditionally have relatively low refractive indices, but they can be raised to technologically useful values. Our group has prepared RI tunable materials up to 1.68 using brominated and aromatic monomers in a copolymer synthesis method. These copolymers are transparent in the technologically important near-IR, have high glass transition temperatures, and are good film formers. These attributes make them useful in optical quality composites where a RI-controlled matrix material is used to match the RI of the incorporated phase to avoid scattering. In addition to composites, applications of these high RI materials include antireflective coatings and high RI lenses, among others.

## INTRODUCTION

Control of refractive index (RI) is extremely important in many optical applications. Transparent composite materials are becoming increasingly important in applications ranging from protective coatings to optical communications. The transparency of such composites can be greatly improved when a RI-controlled matrix material is used to match the RI of the incorporated phase. Antireflective coatings, used on solar cells and lenses, require a range of refractive indices depending on the substrate to be coated. High index materials may be useful for lenses and guiding layers while low index and RI tunable materials can be important in the cladding of waveguiding materials.

Significant contributions have been made to the area of controlled and tunable RI materials. Using sol-gel chemistry, $SiO_2$–$TiO_2$ mixed oxide glasses have been prepared which show a composition-dependent RI from 1.4 to 2.4 [1]. These materials are particularly useful as antireflective coatings for solar cell materials. High refractive index materials for index-matched adhesives have been prepared using brominated and iodinated carbazole rings on a methacrylate backbone [2]. Refractive index was controlled from 1.67 to 1.77 by varying the level of bromination or iodination in the homopolymers. A ternary mixture was studied to lower the melting point of the monomers. Even higher RI polymers, with very high birefringence, were synthesized by the same group using rodlike polymers [3], reaching isotropic RI's as high as 2. Polymers were based on aromatic, rodlike polyamides with 2,2′ substitution over the biphenylene substituents to prohibit crystallization. These materials are targeted for use as polarizing beam splitters, taking advantage of their high birefringence.

We have utilized a technique for making polymers of controlled refractive index through copolymerization. Any refractive index, within the limits of polymers (1.3–1.7+), can be obtained by this method. Using two monomers bracketing the desired RI, a copolymer can be synthesized in which the RI of the copolymer can be varied with the monomer feed composition. The relationship between RI and copolymer composition can be expressed by a simple rule of mixtures to a first approximation. Fine tuning of the monomer feed results in polymers with RI controlled to less than 0.01. The focus of this work is to prepare precisely controlled high RI (1.652) materials using this technique.

Copolymerization to create polymers with tailored RI was explored as part of our work on optical composite materials [4–6]. These composites were constructed by preparing small particles of an optically functional ceramic material and embedding them in a processable, index-matched polymer matrix. The particulate phase studied was Cr-forsterite (Cr-$Mg_2SiO_4$), a solid-state laser material that lases tunably in the technologically important near-IR (1167–1345 nm) in the form of a single crystal. The synthetic method for the Cr-forsterite nanoparticles yielded particles near 100 nm in size which were expected to cause significant Rayleigh scattering unless they were embedded in a matrix of nearly the same refractive index. Using the copolymer method, a polymer matrix material with the average refractive index of Cr-forsterite (1.652 [7]) was synthesized and employed in the optical experiments.

The composite structure resulted in films, rather than single crystals, which exhibited the solid-state laser properties of Cr-forsterite. These films, or fibers prepared using a similar composite structure, would be much more easily integrated into optical communications applications, such as optical amplifiers, than the bulky single crystals. Significant laser amplification of 300 dB/m was demonstrated [5]. The principles used in the development of these composites can be extended to other optically interesting systems such as other solid-state laser materials, nonlinear optical materials, and photochromics. The use of a controlled refractive index matrix material would be important in many of these composites as well as any composite where large inclusions may compromise transparency.

When designing a refractive-index-tuned material, monomers bracketing the desired refractive index must be selected. As is known experimentally and by group contribution theory, aromatic and brominated polymers tend to have higher refractive indices while fluorinated and alkane polymers tend to have lower refractive indices [8]. For many common polymers, RI values can be found in tables; however, calculations may be more appropriate for unusual monomers. In such cases the topological RI calculation developed by Bicerano was found to be extremely useful as a screening method for monomer selection [9]. The monomers selected for this study included napthyl methacrylate (NM), tribromostyrene (TBS), pentabromobenzyl acrylate (PBBA), pentabromophenyl methacrylate (PBPM), and tribromophenyl methacrylate (TBPM), shown in Fig. 1.

Other factors which must be considered in monomer selection for controlled refractive index copolymers depend on the intended application. In our composites, near-IR transparency, compatibility with the ceramic phase, high glass transition temperature ($T_g$), and film forming were all extremely important in addition to the actual refractive index of the matrix. For all of the systems studied, the near-IR transparency was very good and the $T_g$'s were quite high (125–200°C). Compatibilizers were needed to improve the interactions between the particles and the matrix materials and allow good film formation.

Copolymerization was found to be extremely useful in the synthesis of tailored RI materials targeted at 1.652. Polymers such as these are important for the formation of transparent composite materials with relatively large particulate phases like our optical composites. Additionally, RI-tailored materials may be important as

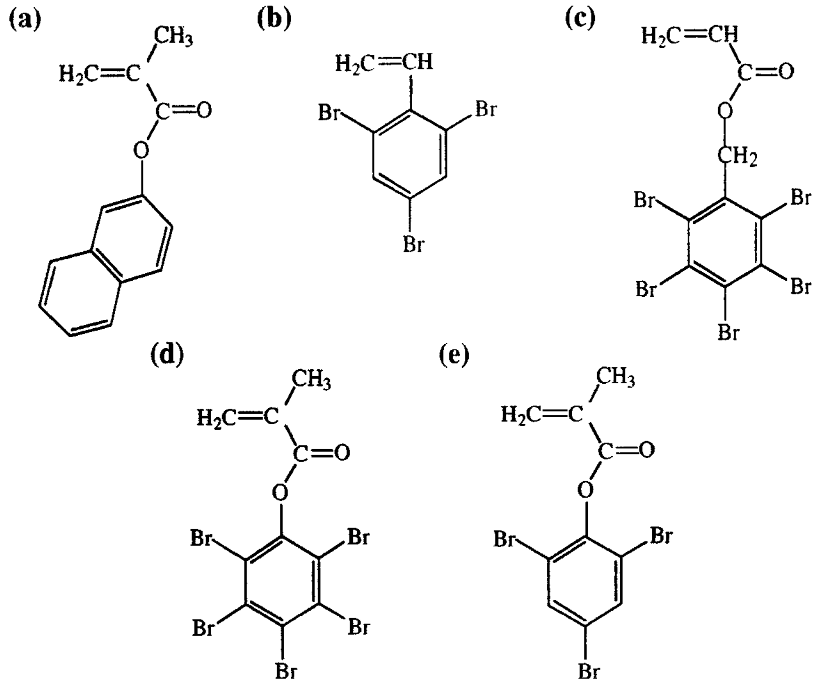

FIG. 1. Structure of high RI monomers: (a) napthyl methacrylate, (b) tribromostyrene, (c) pentabromobenzyl acrylate, (d) pentabromophenyl methacrylate, (e) tribromophenyl methacrylate.

optical elements, antireflective coatings, and waveguide cladding materials among others.

## EXPERIMENTAL

### Synthesis of Napthyl Methacrylate and Pentabromophenyl Methacrylate

NM and PBPM were synthesized using a Schotten-Baumen synthesis, modifying the procedure of Saric et al. [10]. These and other high refractive index monomers have been previously studied for their optical properties [11]. Triethylamine was distilled over $CaH_2$ and both were obtained from Aldrich. Pentabromophenol was obtained from Pfaltz and Bauer. Anhydrous toluene (Sure-seal), 2-napthol, hydroquinone, sodium bicarbonate, sodium sulfite, acetone, heptane, chloroform, chloroform-*d*, and sodium carbonate were obtained from Aldrich and used without further purification. Methacryloyl chloride was used as received from Fluka.

#### Napthyl Methacrylate

Dry glassware was purged with $N_2$. 2-Napthol (33.84 g), hydroquinone (0.257 g), toluene (150 mL), and triethylamine (40.5 mL) were placed in a 3-necked round-bottomed flask, resulting in a clear brown solution. One neck contained a condenser and a $N_2$ inlet, one an addition funnel, and the third was sealed with a septum. The addition funnel was charged with toluene (25 mL) and methacryloyl chloride (28 mL). The reaction vessel was lowered into a water bath to which ice could be added if the temperature increased. The methacryloyl chloride solution was added dropwise at a rate of about 30 drops/min while the reaction mixture was stirred magnetically. The cloudy, light orange mixture was allowed to stir at room temperature overnight. The solution was filtered using a Buchner funnel, resulting in a creamy white solid and a cloudy orange liquid. The liquid was washed 5 times with a water/sodium bicarbonate mixture, then dried over sodium sulfite. The orange liquid was filtered through a Buchner funnel, rotary evaporated to dryness, and dried under vacuum overnight, resulting in a tan solid (55.21 g). The material was purified using column chromatography (2% acetone in heptane, silica gel column) and the pure fractions were rotary evaporated to dryness and dried under vacuum overnight, resulting in a white powder (33.6%). IR of the powder showed the following peaks in $cm^{-1}$: 1728 (carbonyl), multiple peaks from 2924 to 3051 (aromatic C—H, $-CH_3$, vinyl —CH), 750 and 808 (aromatic C—H), and 1637 (—C=C—). NMR of the product in $CDCl_3$ showed the following shifts in ppm: 2.10 ($CH_3$), 5.79 (vinyl), 6.41 (vinyl), multiple peaks 7.25-7.88 (aromatic). IR and NMR characterization have not been previously reported for this monomer to the author's knowledge. The melting temperature of the monomer was measured as 64-66°C. This correlates well with 66°C measured by Hadjichristidis et al. [12].

#### Pentabromophenyl Methacrylate

PBPM was prepared in a similar manner. The reaction vessel was charged with pentabromophenol (9.69 g), toluene (45 mL), and triethylamine (3.5 mL), resulting in a yellowish brown solution. Toluene (5 mL) and methacryloyl chloride (2.4 mL) were added to the addition funnel. The methacryloyl chloride solution was added at about 20 drops/min and resulted in a bright yellow cloudy solution. The solution was filtered through a Buchner funnel, resulting in a creamy white solid and clear bright yellow solution. It was then washed with sodium bicarbonate in water 5 times, dried over sodium carbonate, rotary evaporated to dryness, and dried overnight under vacuum, yielding a yellowish green chunky, sticky product (9.3095 g). The material was purified using column chromatography (15% chloroform in heptane, silica gel column), and the pure fractions were rotary evaporated to dryness and dried under vacuum overnight, resulting in a white powder (70%). IR of the powder showed the following peaks in $cm^{-1}$: 1737 (carbonyl), multiple peaks from 2854 to 2995 ($-CH_3$, vinyl $-CH$), 1099 (aromatic Br), and 1633 ($-C=C-$). NMR of the product in $CDCl_3$ showed the following shifts in ppm: 2.10 ($CH_3$), 5.89 (vinyl), and 6.47 (vinyl). IR has not been previously reported, and the NMR is slightly shifted from that reported by Saric et al. (1.88, multiple signals 5.36-6.30) [10]. A melting point of 142–143°C was measured which compares well with the melting point of 138–140°C measured by Sumrell et al. [13].

## Synthesis of the Tailored RI Copolymers

NM and PBPM were prepared as described above. In some experiments NM from Dajac Monomer and Polymer Laboratories was used after multiple recrystallizations from petroleum ether (Fisher). Tribromostyrene and pentabromobenzyl acrylate were graciously provided by Jerry Garrison at AmeriBrom and were used without further purification. Tribromophenyl methacrylate (Polysciences) was used without further purification. $\alpha,\alpha'$-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol/acetone. Anhydrous toluene (Sure-seal) and lauryl mercaptan were obtained from Aldrich and used as received.

Polymerizations were performed in dry test tubes or small round-bottomed flasks under $N_2$ with magnetic stirring. The amounts of each monomer were varied as shown in Table 1. In a typical polymerization, the test tube was charged with the monomers (~2 g) and AIBN (0.2 wt%), closed with a rubber septum, and purged with $N_2$. Anhydrous toluene (~20 mL) was added, and the solution was degassed with $N_2$ for 15-20 minutes. It was then lowered into a 60°C bath and left to polymerize overnight. The polymer solution (in some cases some polymer precipitated) was precipitated in methanol. The resulting polymer was recovered by filtration, dissolved into toluene again (typically this required heat), reprecipitated, recovered again, dried overnight under vacuum, and yielded a white, tan, or yellow powder. The molecular weight was controlled in a few cases through the addition of lauryl mercaptan (lowers MW) or less AIBN (raises MW).

Target copolymer compositions could be calculated using a simple rule of mixtures approximation shown in Eqs. (1) and (2). For example, a composition of 75/25 TBS/NM ($RI_{tbs}$ = 1.660, $RI_{nm}$ = 1.632) was expected to result in the target RI of 1.653 for the optical composites. Some fine tuning of the monomer feed composition was generally needed to achieve exact RIs.

$$(\text{mol\% A}) * (\text{RI A}) + (\text{mol\% B}) * (\text{RI B}) = \text{target RI} \tag{1}$$

$$\text{mol\% A} + \text{mol\% B} = 1 \tag{2}$$

## Characterization

The Becke line technique [14] was used to measure the refractive index of the copolymers using RI matching oils (0.002 increments) and an optical microscope equipped with a sodium D line filter (589.3 nm). Elemental analysis for bromine as

TABLE 1. Summary of Copolymers Synthesized[a]

| Starting composition | NM, g | Br monomer, g | AIBN, mg | Toluene, mL | Lauryl mercaptan, $\mu$L | Yield, % | $M_w$ (× $10^3$)/PDI |
|---|---|---|---|---|---|---|---|
| 100% NM | 2.1798 | | 4 | 20 (B) | | 54 | 77/2.2 |
| | 2.0027 | | 5.6 | 27 | | 67 | 63/2.6 |
| PBPM/NM: | | | | | | | |
| 25/75 | 1.0822 | 0.9465 | 5.0 | 20 | | 38 | 23/2.1 |
| 50/50 | 0.5416 | 1.4206 | 5.8 | 15 | | 13.7 | 10/1.8 |
| | 0.5414 | 1.4195 | 5.6 | 15 | | 13.2 | 19/2.4 |
| 75/25 | 0.2711 | 2.130 | 5.5 | 15 | | 16 | 5.8/1.5 |
| 95/5 | 0.0730 | 3.5968 | 6.6 | 15 | | 8.3 | 6/1.4 |
| PBBA/NM: | | | | | | | |
| 20/80 | 1.1549 | 0.7575 | 5.9 | 20 | | 67 | 37/2.1 |
| 25/75 | 1.0829 | 0.9464 | 5.0 | 20 | | 39.4 | |
| 40/60 | 0.8666 | 1.5148 | 5.2 | 20 | | 69 | 33/2 |
| 50/50 | 0.5416 | 1.4204 | 5.0 | 15 | | 40.2 | 31/1.7 |
| | 1.0828 | 2.8398 | 9.3 | 30 | | 70.5 | Insoluble |
| | 0.5414 | 1.4199 | 5.5 | 15 | | 73 | 31/2.4 (P) |
| | 0.5246 | 1.4202 | 5.3 | 15 | 46.0 | 85 | 9/1.7 |
| | 0.2713 | 0.7106 | 2.9 | 7.5 | 11.6 | 75.8 | 11.5/1.9 (P) |
| | 0.2711 | 0.7102 | 2.4 | 7.5 | 5.8 | 77.8 | 13.7/2.1 (P) |
| 60/40 | 0.4334 | 1.7037 | 5.4 | 15 | | 76 | 13/2. 7 (P) |
| 75/25 | 0.2707 | 2.1294 | 5.3 | 15 | | 73 | Insoluble |
| | 0.1359 | 1.0652 | 2.7 | 7.5 | 42.6 | 84.9 | 4/1.4 (P) |
| | 0.1354 | 1.0657 | 2.4 | 7.5 | 28.4 | 81.5 | Insoluble |
| | 0.1357 | 1.0656 | 2.8 | 7.5 | 12 | 86.2 | Insoluble |
| 95/5 | 0.0721 | 3.5962 | 5.2 | 15 | | | Insoluble |
| 100/0 | | 1.8932 | 5.7 | 20 | | 68 | Insoluble |
| TBS/NM: | | | | | | | |
| 50/50 | 0.7214 | 1.1588 | 6.2 | 20 | | 64 | 61/2 |
| 55/45 | 2.4 | 4.7109 | 15.0 | 75 | | 58 | 50/2.1 |
| | 2.0097 | 3.9257 | 10.5 | 40 | | 77.8 | 107/4.2 |
| | 1.9950 | 3.9242 | 4.9 | 20 | | 81.1 | 781/10.3[b] |
| 75/25 | 0.2709 | 1.3043 | 5.4 | 15 | | 79 | 33/2. 3 |
| 95/5 | 0.0540 | 1.6511 | 4.9 | 15 | | 52.8 | 46/1.7 |
| 100/0 | | 2.3040 | 5.5 | 20 | | 88 | 137/4 (P) |
| TBPM/NM: | | | | | | | |
| 75/25 | 0.2705 | 1.5259 | 5.9 | 15 | | 23 | 9.8/1.7 |
| 95/5 | 0.0545 | 1.9328 | 5.7 | 15 | | 3.4 | 9.3/1.9 |
| 100/0 | | 2.7123 | 5.4 | 15 | | | 9.9/1.8 |

[a] $M_w$ = weight-average molecular weight and PDI = polydispersity measured by gel permeation chromatography compared to polystyrene standards; B = benzene was used as solvent; insoluble = not soluble in THF; P = partially dissolved in THF.

[b] Copolymer used in optical experiments.

well as carbon and hydrogen (Scandinavian Microanalytical Laboratory, Herlev, Denmark) was used to measure the composition of the copolymers.

Measured copolymer compositions were calculated from the elemental analysis for Br and confirmed with the C and H measurements taken at the same time. Equations (3)-(5) show the relationships between the measured wt% Br content and the Br monomer composition for (3) PBPM/NM and PBBA/NM copolymers, (4) TBS/NM copolymers, and (5) TBPM/NM copolymers.

$$\text{mol fraction PBBA or PBPM} = \frac{212.2\ (\text{measured }\%\text{Br})}{399.5 - 344.5\ (\text{measured }\%\text{Br})} \tag{3}$$

$$\text{mol fraction TBS} = \frac{212.2\ (\text{measured }\%\text{Br})}{239.7 - 128.6\ (\text{measured }\%\text{Br})} \tag{4}$$

$$\text{mol fraction TBPM} = \frac{212.2\ (\text{measured }\%\text{Br})}{239.7 - 186.6\ (\text{measured }\%\text{Br})} \tag{5}$$

Molecular weights were measured using a Waters gel permeation chromatography system (510 pump, 712 WISP, 490 UV detector) and compared to polystyrene standards. The thermal properties were examined using differential scanning calorimetry on a TA Instruments DSC 910. Near-IR measurements were made on a Varian Cary 5 UV-Vis-NIR spectrophotometer. Monomers and copolymers were also examined using a Mattson Instruments Galaxy 2020 FTIR spectrophotometer and a Varian 400 MHz NMR spectrometer.

## RESULTS/DISCUSSION

Using Bicerano's method, high RI monomers were selected for the Cr-forsterite composites [9]. Napthyl methacrylate was selected as the low index monomer while pentabromophenyl methacrylate, tribromophenyl methacrylate, pentabromobenzyl acrylate, and tribromostyrene were promising choices as high index monomers bracketing 1.652. Table 2 summarizes the calculated and measured refractive indices of these monomers, and Fig. 1 shows the structure of the monomers. Close examination of the table shows that in some cases the calculation was ex-

TABLE 2. Calculated and Experimental RIs for High Index Monomers

| Homopolymer | Calculated RI | Experimental RI |
|---|---|---|
| NM | 1.634 | 1.632 |
| PBPM | 1.707 | 1.71[a] |
| PBBA | 1.684 | 1.670 |
| TBPM | 1.653 | 1.660 |
| TBS | 1.707 | 1.660 |

[a] Homopolymer could not be synthesized; value from Ref. 9.

tremely accurate (NM); however, in others only an approximate value was obtained. This can be expected as the calculation was derived empirically. By copolymerizing the brominated monomers with napthyl methacrylate, the refractive index was controlled by the composition of the copolymers. All systems studied could be used to produce materials with the target refractive index of 1.65, near-IR transparency, and high glass transition temperatures. Of all the systems, the TBS/NM system showed the best film-forming properties, and was ultimately chosen for all composite experiments.

## Composition

Figure 2 summarizes the composition results obtained by elemental analysis. The straight line represents a one-to-one correlation between the feed monomer composition and final copolymer composition. The composition of the resulting copolymers varied slightly from the starting values, probably due to slight variations in the reactivity of the monomers. If the yield of the polymerizations was 100%, this variation would be minimized. The yields of the copolymers are relatively low after purification, as shown in Table 1. This may be due to chain transfer caused by the brominated monomers, resulting in a large fraction of low molecular weight material that was washed away during purification.

For the PBBA/NM and TPBM/NM copolymers, the measured Br monomer composition was only slightly less than the starting feed composition. The homopolymer compositions also showed low measured Br contents, which may indicate some residual organic material was introduced during work-up of the polymers. In PBPM/NM copolymers, which showed very low yields, a significant preference to

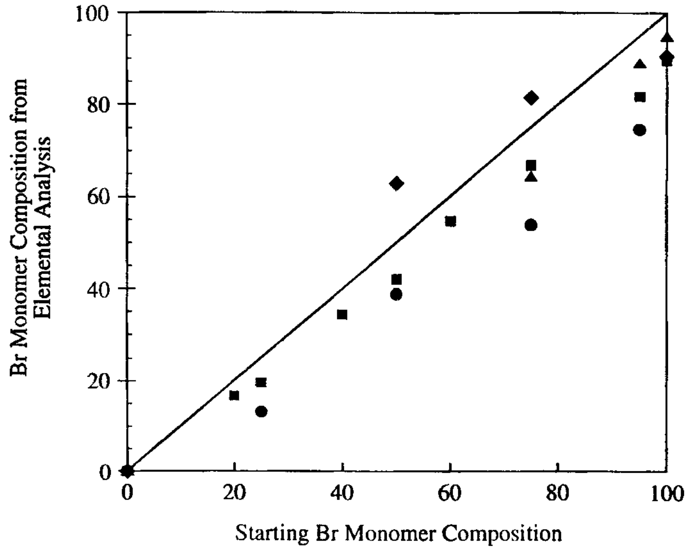

FIG. 2. Starting composition vs measured composition in terms of Br monomer: PBBA/NM copolymers (■), TBS/NM copolymers (◆), PBPM/NM copolymers (●), TBPM/NM copolymers (▲).

incorporate NM into the copolymer was seen. Although the yields were higher, the TBS/NM copolymers tended to incorporate excess TBS. Because the starting feed compositions did not give precise results, particularly with the PBPM- and TBS-containing copolymers, the rule of mixtures was used as an estimate of necessary feed composition. Fine tuning of the monomer feed composition easily resulted in refractive indices controlled to less than 0.01.

FT-IR was used to confirm the elemental analysis results. Figure 3 shows a comparison of several compositions in the TBS/NM system. The peak at 1748 $cm^{-1}$, representing the carbonyl group in NM, increased as expected with increasing NM content. The peak at 1030 $cm^{-1}$, representing Br attached to the aromatic ring in TBS, decreased in intensity as the amount of TBS in the copolymer was decreased. Clearly these characteristic peaks of the poly(tribromostyrene) and poly(napthyl methacrylate) were combined in the resulting copolymers.

Composition of the PBPM/NM copolymers was evaluated by NMR, but the results were not consistent with the elemental analysis results, possibly due to spectrum phasing or long relaxation times. Most PBBA/NM copolymers were insoluble in common organic solvents so that NMR could not be performed. The TBS/NM and TBPM/NM copolymers could not be evaluated by NMR because of the overlap of peaks in both the aromatic and backbone regions.

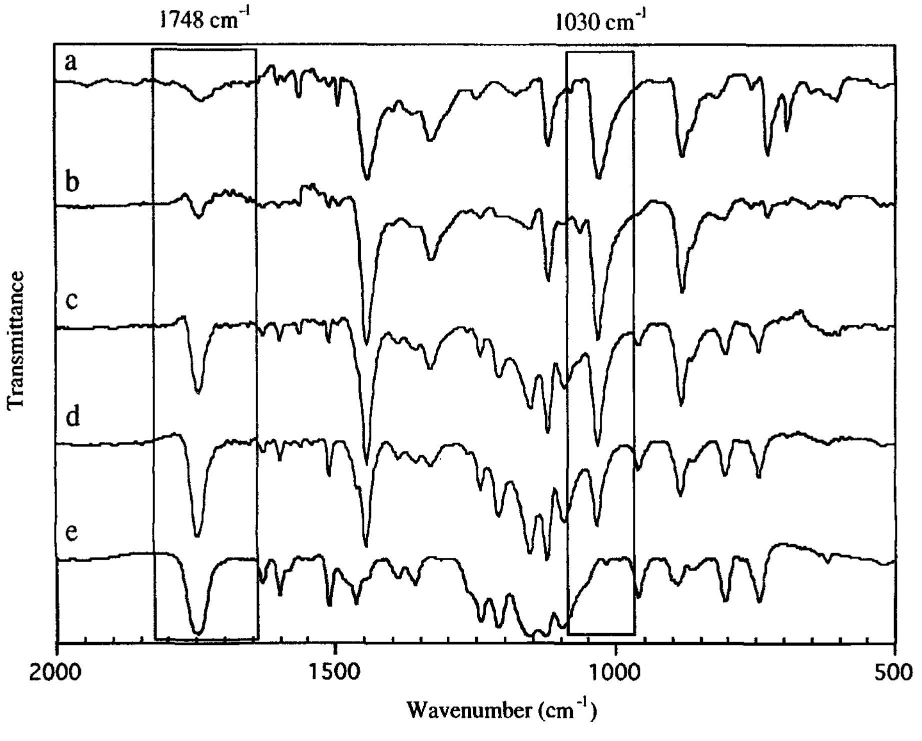

FIG. 3. IR comparison of TBS/NM copolymers: a) poly(tribromostyrene), b) 95/5 TBS/NM copolymer, c) 75/25 TBS/NM copolymer, d) 50/50 TBS/NM copolymer, e) poly(napthyl methacrylate).

## Physical Properties

### Molecular Weight

Molecular weight is very important in applications where good mechanical properties of the RI-tuned polymer are desired. In general, mechanical properties improve with increasing molecular weight of the polymer. In our composites, the copolymer matrix needed to have good film-forming properties, which required molecular weights above the entanglement molecular weight (typically above 30,000 g/mol). Experimentally, the highest molecular weight copolymers prepared (780,000 g/mol) showed the best film-forming properties.

The copolymer weight-average molecular weights ($M_w$) and polydispersities (PDI) are summarized in Table 1. NM homopolymer showed reasonable molecular weights for film formation. The PBPM/NM copolymers showed very low molecular weights, which became lower with increasing PBPM content. Similarly the TBPM/NM copolymers showed unacceptably low molecular weights for the film applications. The PBBA/NM copolymers had severe solubility problems in THF, as well as many common organic solvents, which made few compositions useful for the composite experiments. Attempts to lower molecular weight and increase solubility using lauryl mercaptan as a chain transfer agent resulted in unacceptably low molecular weights in this system. The TBS/NM system had the highest molecular weights, and accordingly showed the best film-forming properties. Because of this, the TBS/NM system was chosen for all optical composite experiments, and higher molecular weight copolymers were synthesized to further improve film formation.

### Glass Transition Temperatures

Glass transition temperature is important depending on the application of the RI-controlled polymer material. For our composites, high $T_g$s were required to improve stability, particularly during the optical experiments when some sample heating occurred. All of the high RI copolymers showed relatively high glass transition temperatures (125–200°C), which were desirable in the optical composites. Figure 4 shows the glass transition temperature as a function of composition for the TBS/NM system. The copolymer glass transition temperature increased with increasing TBS content as expected.

## Optical Properties

### Refractive Index

For the composite applications, good control of the polymer RI was critical to prevent Rayleigh scattering. The refractive index (at 589.3 nm) as a function of composition measured from elemental analysis is shown graphically for all four high index copolymer systems in Fig. 5. Clearly the copolymer refractive indices were bracketed by the refractive indices of the starting monomers, and the target refractive index of 1.652 could be obtained by controlling the composition in all systems studied. A linear rule of mixtures relationship (dashed line) was a good first approximation of the expected RI, and could be fine tuned with the specific monomer system used. The small window of RI that was bracketed (0.06) for these

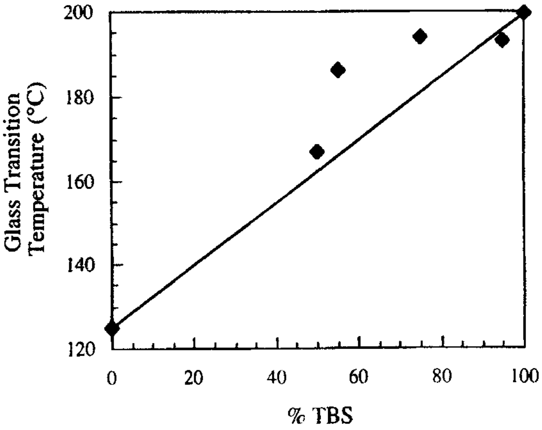

FIG. 4. Glass transition temperature vs starting composition for TBS/NM copolymers. The line represents the expected behavior if the linear rule of mixtures were used to determine the $T_g$.

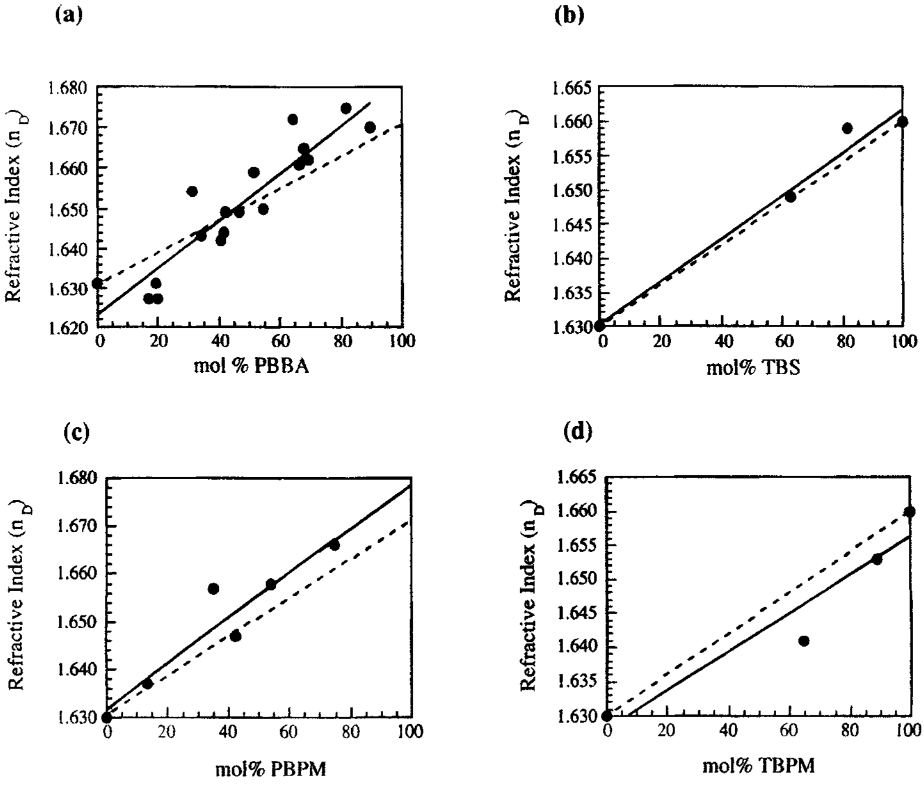

FIG. 5. RI vs composition (measured from elemental analysis) for all four high index copolymer systems: (a) PBBA/NM, (b) TBS/NM, (c) PBPM/NM, (d) TBPM/NM. The solid curves represent the best linear fits to the data. The dashed curves represent the expected behavior following the rule of mixtures.

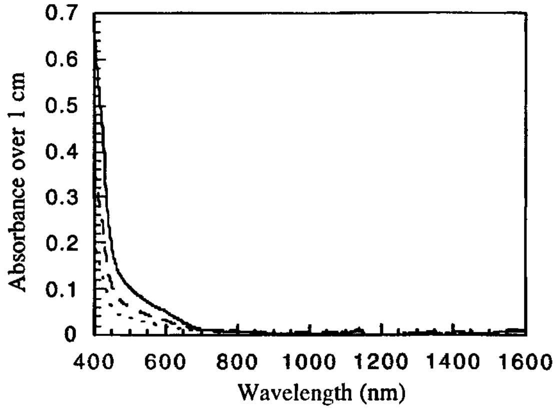

FIG. 6. Near-IR absorbance of a PBBA/NM copolymer: 2.5% (dotted), 5% (dashed), and 10% (solid) solutions in THF.

copolymers accentuated tiny fluctuations in composition measurements, resulting in scatter from the expected linear relationship.

### Near-IR Transparency

In the design of RI-tuned materials for optical applications, transparency at the experimental wavelengths used is extremely important. The experiment for our high index copolymer composites had two critical wavelengths for which the matrix needed to be transparent. The composite was pumped with laser light at 1.06 $\mu$m and amplified between 1.2–1.3 $\mu$m, thus absorption by the polymer at these wavelengths could complicate the amplification results and might result in damage to the polymer.

Figure 6 shows the near-IR absorption of 2.5, 5, and 10% solutions of a 31/69 PBBA/NM copolymer in THF. As these polymers needed to be transparent over long distances (cm) for the optical experiments, solutions were used (10% over 1 cm may be equated to 1 mm of polymer) rather than films ($< 10$ $\mu$m thick). Clearly the polymer had no significant absorption at either of the critical wavelengths (1.06 $\mu$m, 1.2–1.3 $\mu$m). Nearly identical spectra could be seen for the TBPM/NM, PBPM/NM, and TBS/NM copolymers. Although THF absorbs in this region of the spectrum, the effects were removed using a reference. The transparency was confirmed in the composite experiments, as TBS/NM copolymer matrix samples did not show damage after repeated exposure to the laser.

## CONCLUSIONS

Copolymerization of monomers bracketing the target RI value was found to be extremely useful in the creation of controlled, high refractive index materials for optical composite applications. Monomers with refractive indices near 1.65 were selected using empirical calculation methods. Monomer selection affected other important properties of the copolymers used including transparency, glass transition temperature, and compatibility. Molecular weight of the copolymers was also important in the formation of high quality films.

A simple rule of mixtures relationship was used to determine approximate monomer feed composition, and further refining of the monomer feed yielded highly controlled RI materials to less than 0.01 from the target RI. Several high RI (1.652) systems were studied, and suitable monomers were available or could easily be synthesized. All copolymer systems synthesized could obtain the target RI, were transparent in the near-IR, and had high $T_g$s. The TBS/NM copolymers were the most desirable for the targeted optical composite structure due to their high molecular weight and good film-forming ability.

Applications for these high RI materials may include antireflective coatings, high RI lenses, and the composite applications discussed in this paper, among others. The copolymerization method allowed excellent control of RI in the unusually high RI materials necessary for optical composite applications.

## ACKNOWLEDGMENTS

We are grateful to the National Science Foundation, Department of Education, and Cornell Materials Science Center for support of this project. Thank you to Jerry Garrison from AmeriBrom for providing two monomers used in this study.

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Received May 10, 1996
Revision received August 20, 1996