Thermooptical Properties of Poly(methyl methacrylate)-Based Azobenzene Composites

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ABSTRACT: In this article, poly(methyl methacrylate)-based azobenzene composites were prepared. The temperature coefficient of the refractive index of these composites was investigated. The dependence of the temperature coefficient of the refractive index on the azobenzene chromophore concentrations was studied experimentally. These optically interesting thermal parameters are very useful in material optical applications, thermooptical polymeric switches, and waveguide technology. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2374–2377, 2003

INTRODUCTION

Integrated optics plays an important role in several areas of optical communications, such as in advanced information processing, optoelectronic interconnections, and fiber-optic communications.[1–4] High-performance switches are important devices to fully utilize the opportunities provided by integrated optics. Polymer thermooptic (TO) switches have an advantage in that they require only a low driving electric power to operate because polymers have a large thermooptic coefficient and low thermal conductivity.[5–7] In recent years, polymer TO switches have attracted much attention because their fabrication process is simple and cost-effective.[8,9]

The magnitude of the refractive index variation as a function of temperature, namely, the temperature coefficient of the refractive index, is a very important property for TO polymer materials. The temperature coefficient of the refractive index in inorganic glasses is less than 10^{-5} °C^{-1}, while it is 4×10^{-5} °C^{-1} for $LiNbO_3$. The temperature dependence of the refractive index in glasses and $LiNbO_3$ is due to the changes of both the density and the absorption band.[10,11] However, as for organic polymers, the temperature dependence of the refractive index is almost exclusively from the density change.[10,12] This is why most organics have a negative temperature coefficient of the refractive index. In some applications, polarization insensitivity is of key importance, but conventional $LiNbO_3$ switches are polarization-sensitive, while polymeric TO switches have the advantage of being polarization-insensitive. Hence, wide applications of polymeric TO materials in modern communication systems are anticipated. Therefore, the study of the optically related thermal properties of polymer materials is very important from the practical viewpoint.

In this article, poly(methyl methacrylate) (PMMA)–azobenzene chromophores composites were prepared. The composites' TO properties were investigated experimentally. The doping concentration dependence of the composites' TO properties was investigated as well.

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EXPERIMENTAL

Sample preparation

PMMA (M_W = 93,000), 4′-(2-hydroxyethyl)ethylamino-2-chloro-4-nitroazobenzene (Disperse Red 13, DR 13), 4′-(2-hydroxyethyl)ethylamino-4-nitroazobenzene (Disperse Red 1, DR 1), and 4′-bis-hydroxyethylamino-4-nitroazobenzene (Disperse Red 19, DR 19) were purchased from the Aldrich Chemical Co.

The samples were prepared as follows: PMMA was dissolved in toluene. A clear solution was obtained. To this clear solution, a DR 13, DR 1, or DR 19 solution in toluene was added. Then, the mixture was stirred for

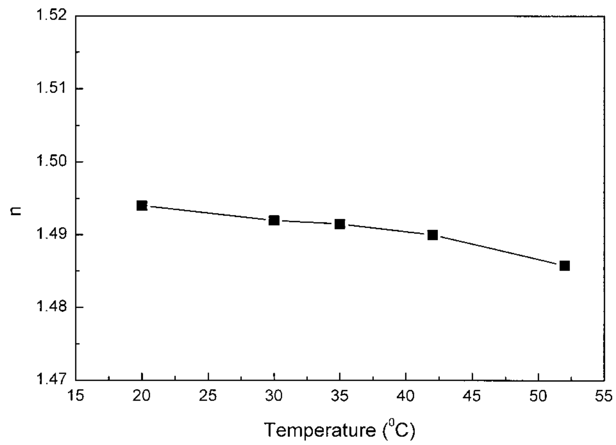

Figure 1 Refractive index of pure PMMA film at different temperatures.

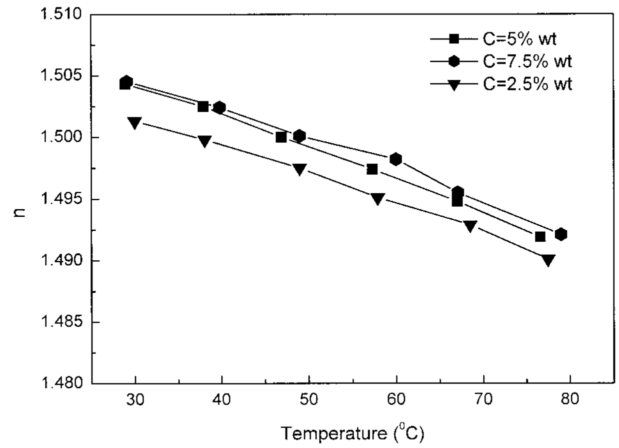

Figure 2 Refractive index as a function of temperature for PMMA–DR 1 composites.

20 min. Afterward, the solution was filtered (5.0 μm, Teflon) into another beaker. Later, the solution was heated on a hot plate to evaporate some of the solvents. After the solution volume was reduced to about 3 mL, the film samples were cast from the solutions on the prism of an Abbe refractometer.

Measurement

The refractive index was measured by using an Abbe refractometer. The temperature was controlled with a thermostat.

RESULTS AND DISCUSSION

Figure 1 shows the refractive index of a pure PMMA film sample at different temperatures. It can be seen that the refractive index of the sample decreases with increasing temperature, namely, the sample has a negative temperature coefficient of the refractive index. For most polymer materials, the temperature dependence of the refractive index comes from the density change; hence, most polymers have negative temperature coefficients, and PMMA is no exception.

The refractive index of the composite systems was measured at different concentrations. Figures 2, 3, and 4 show the refractive index as a function of temperature for the PMMA–DR 1 composites (PMMA–DR 1), PMMA–DR 13 composites (PMMA–DR 13), and PMMA–DR 19 composites (PMMA–DR 19), respectively. As seen in these figures, the composites' refractive indexes decrease with increasing temperature, and the composites' refractive index variation can be realized by changing the azobenzene chromophore concentration in the polymer sample. It is well known that, as for waveguide techniques, the matching of the refrac-

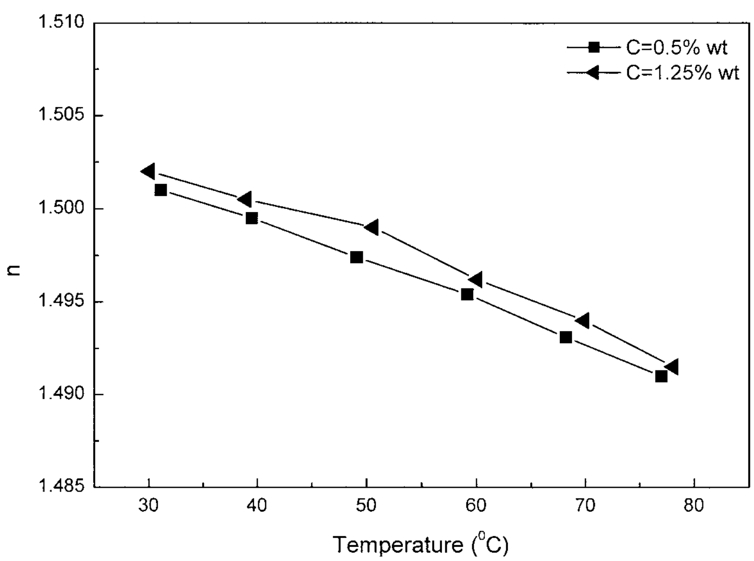

Figure 3 Refractive index as a function of temperature for PMMA–DR 13 composites.

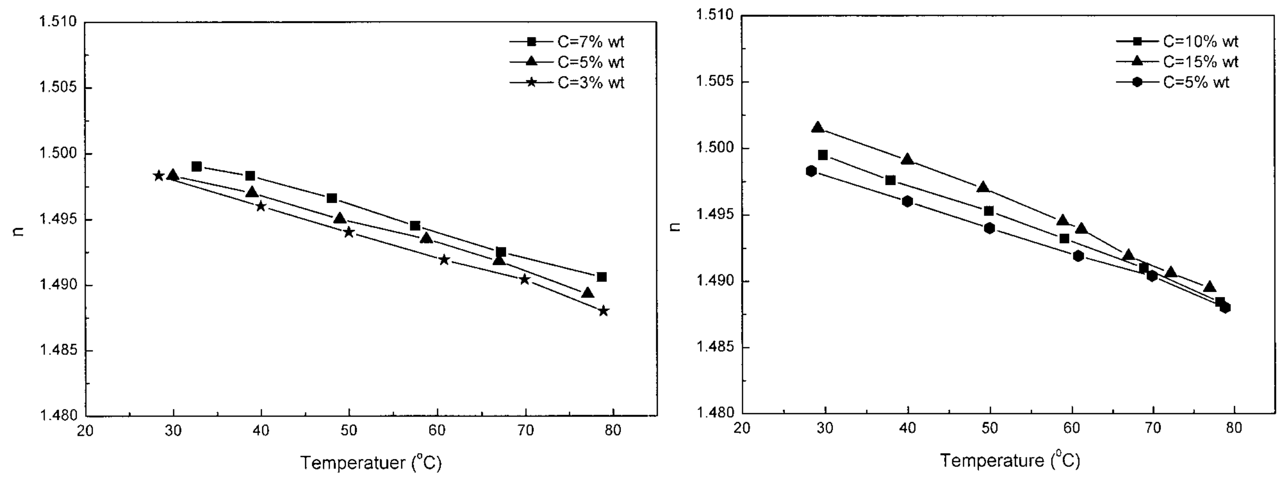

Figure 4 Refractive index as a function of temperature for PMMA–DR 19 composites.

tive index between the core layer and the cladding layer is critical; hence, precise refractive index control for TO polymer materials is of importance. In the composite systems, about 1% of the refractive index variation can be achieved by doping. Also, the refractive index of the composite systems can be adjusted by controlling the doping concentration.

Tables I–III show the refractive index under different concentrations at 30°C and the TO coefficient (TOC = $-dn/dt$) for the composite systems. From these tables, it can be seen that the refractive index of the composite systems increases with an increasing chromophore concentration. For the PMMA–DR 19 system, the TOC generally increases as the chromophore concentration is increased, while for the PMMA–DR 1 and PMMA–DR 13 systems, the TOC decreases slightly with an increasing doping concentration. This may be due to the DR 1 and DR 13 molecules having higher polarity and being easier to aggregate, in particular, at higher doping concentrations. The dependence of the TOC on the doping concentration is also very interesting and an important observation from the standpoint of the designing of TO materials and devices.

TABLE I
Refractive Index Under Different Concentrations at 30°C and the TOC for the PMMA–DR 1 Composite System

Parameter	*C* (wt %) 2.5%	5%	7.5%
n	1.5012	1.5041	1.5043
TOC = $-dn/dt$ (°C^{-1})	2.610×10^{-4}	2.465×10^{-4}	2.465×10^{-4}

TABLE II
Refractive Index Under Different Concentrations at 30°C and the TOC for the PMMA–DR 13 Composite System

Parameter	*C* (wt %) 0.5%	1.25%
n	1.5011	1.5019
TOC = $-dn/dt$ (°C^{-1})	2.186×10^{-4}	2.176×10^{-4}

CONCLUSIONS

In the present study, PMMA–DR 1, PMMA–DR 13, and PMMA–DR 19 composite systems were prepared. The TOCs of these composite systems were measured. The composite systems show negative TOCs, and the refractive indexes of the composite systems can be adjusted by controlling the doping concentration. For the PMMA–DR 19 system, the TOC generally increases as the chromophore concentration is increased, while for the PMMA–DR 1 and PMMA–DR 13 systems, the TOC decreases slightly with an increasing doping concentration. These optically interesting thermal parameters are very useful for TO material applications and waveguide technology.

TABLE III
Refractive Index Under Different Concentrations at 30°C and the TOC for the PMMA–DR 19 Composite System

Parameter	*C* (wt %) 3%	5%	7%	10%	15%
n	1.4977	1.4982	1.4992	1.4994	1.5013
TOC = $-dn/dt$ (°C^{-1})	1.992×10^{-4}	1.900×10^{-4}	1.886×10^{-4}	2.242×10^{-4}	1.559×10^{-4}

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