Polymer Bulletin 58, 145–151 (2007)
DOI 10.1007/s00289-006-0516-4

Polymer Bulletin

Comparison of optical properties of thermally reversible light scattering films consisting in dispersions of polystyrene/naphthalene domains or polystyrene/liquid crystal (EBBA) domains in epoxy matrices

I. A. Zucchi, T. Resnik, P. A. Oyanguren, M. J. Galante(✉), R. J. J. Williams

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and
National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina
T. Resnik was on leave from Universidad Simón Bolívar, Venezuela
E-mail: galant@fi.mdp.edu.ar; Fax: +54-223-4810046

Received: 5 July 2005 / Accepted: 11 January 2006

Summary

Thermally reversible light scattering (TRLS) films are materials that can be reversibly switched from opaque to transparent states by varying temperature. TRLS films containing different types of dispersed domains in an epoxy matrix: a) naphthalene/polystyrene (NP/PS), and b) liquid crystal (EBBA/PS), were synthesized by polymerization-induced phase separation. The intensity of transmitted light was measured as a function of temperature in successive heating/cooling cycles. Transparent states were observed during heating cycles at temperatures close to the melting point of NP (81 ºC) or the nematic-isotropic transition of EBBA (at about 70 ºC). The NP crystallization from their polystyrene solutions in the course of cooling cycles required large undercooling (about 30 ºC). In the temperature range comprised between melting and crystallization, optical properties depend on the cooling rate and the thermal history of the material. The situation was quite different for TRLS films based on EBBA. In this case, the generation of a nematic phase from the polystyrene solution required a small undercooling (about 2 - 3 ºC), leading to a relatively sharp transition between opaque and transparent states, independent of the thermal history. This constitutes a significant advantage of the use of liquid crystals compared to organic crystals in the manufacture of TRLS films.

Introduction

Thermally reversible light scattering (TRLS) films are materials that can be reversibly switched from opaque to transparent states by varying temperature. They have potential applications in thermal sensors, optical devices, recording media and several other applications [1-4]. In most cases these materials are based on multiphase blends

---

Presented at 44th P.M.M. Microsymposium "Polymer Gels and Networks",
Prague, 10–14 July 2005

with one of the phases undergoing an order-disorder transition at a particular temperature. In the isotropic (disordered) state every phase has the same refractive index and the material is transparent. In the ordered state there is a mismatching of refractive indices and the material is opaque.

In recent papers we showed that TRLS films consisting in dispersions of diphenyl (DP)/polystyrene (PS) domains or *N*-4-ethoxybenzylidene-4'-*n*-butylaniline (EBBA)/ PS domains in epoxy matrices, could be synthesized in one step by polymerization-induced phase separation [5-7]. As PS is slightly compatible with the epoxy precursors but miscible in all proportions with the organic crystal (DP) or the liquid crystal (EBBA), above their melting or nematic-isotropic transition temperatures, a small amount of PS added to the initial solution produced phase separation of DP/PS or EBBA/PS domains during the polymerization reaction. This enabled to generate dispersions with primary morphologies that remained stable in the course of successive heating-cooling cycles. The order-disorder transition was confined to the interior of the dispersed domains that act as light-scattering centers of the TRLS films. The refractive indices of DP and EBBA in the amorphous state were the same as those of PS and the cured epoxy matrix. Therefore, in spite of being optically heterogeneous TRLS films were transparent above the melting temperature of DP or the nematic-isotropic transition temperature of EBBA. The films became opaque when the DP crystallized or EBBA was transformed to the nematic state in the interior of dispersed domains, due to the mismatching of refractive indices.

Aims of this paper are to analyze optical properties of materials based on naphthalene (NP) as organic crystal and to compare them with those of TRLS films based on EBBA.

Experimental

Materials

The epoxy monomer was based on diglycidilether of bisphenol A (DGEBA, Der 332, Dow), with a mass per mol of epoxy groups equal to 174.3 g mol^{-1}. The aliphatic diamine was meta-xilylenediamine (MXDA, Aldrich). The crystalline solid naphthalene (NP, Aldrich) characterized by the following melting point: Tm = 81 °C, was used as received. A commercial monodisperse polystyrene was employed (PS, Mn = 28400 g mol^{-1}, IP = 1,045). Their chemical structures are shown in Figure 1.

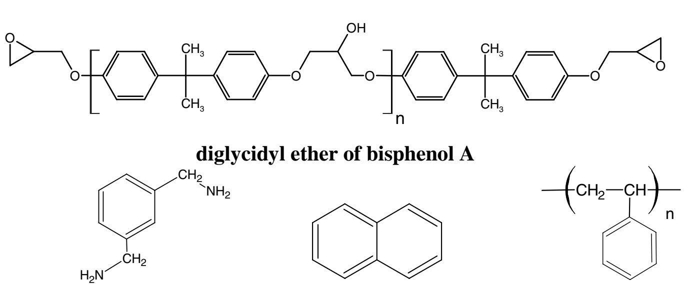


Figure 1. Chemical structures of diglycidyl ether of bisphenol A (DGEBA), *m*-xylylenediamine (MXDA), naphthalene (NP) and polystyrene (PS)

Samples preparation

NP/PS blends were prepared dissolving selected amounts of both components in methylene chloride (CH_3Cl) in order to obtain a homogeneous solution. The solvent was then removed keeping the solution at room temperature, to avoid NP lost. In the absence of a solvent it would have been necessary to heat to about 100 ºC with the risk of NP sublimation.

For reactive NP/PS/DGEBA blends, NP was incorporated to the PS/DGEBA mixture heating at 90 °C, to homogenize the sample. After cooling to room temperature, a stoichiometric amount of amine was added.

Curing schedules

Blends containing 55 wt % of NP and two different PS amounts, 3 and 5 wt % of PS, were cured at 80 ºC up to complete conversion of epoxy groups as assessed by near-infrared spectroscopy (NIR). The complete curing process took 10 hours.

Characterization techniques

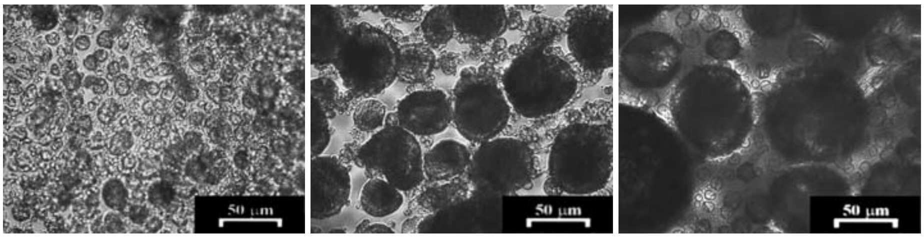
Transmission optical microscopy (TOM) was used to follow the evolution of morphologies after curing. A Leica DMLB microscope provided with a video camera (LEICA DC 100) and a hot stage (Linkman THMS 600) was employed. Optical transmittance measurements in the wavelength of visible light were made using a photodetector incorporated into the optical path of the microscope.

Differential scanning calorimetry (DSC, Pyris 1, Perkin-Elmer) was used in order to determine the thermal transitions that occur during cooling and heating cycles, at 10 °C min^{-1} under nitrogen. The samples were first heated to 80 °C, cooled at 10 °C min^{-1} to a temperature below the transitions to be determined and then heated at the above mentioned rate.

The glass transition temperature (Tg) was defined as the onset of the change in the specific heat. The melting temperature (Tm) was taken at the end of the endothermic peak, corresponding to the temperature at which the last fraction of crystals was dissolved.

Results and Discussion

Morphologies generated in films synthesized using naphthalene (NP) are shown in Figure 2 for different compositions (55 wt % NP and 1, 3 and 5 wt % PS). They are

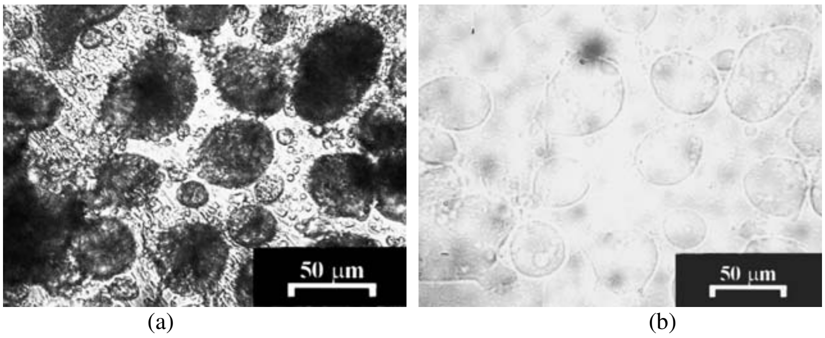


(a) (b) (c)

Figure 2. TOM micrographs obtained at room temperature for TRLS films synthesized using: a) 55 wt % NP and 1 wt % PS; b) 55 wt % NP and 3 wt % PS; c) 55 wt % NP and 5 wt % PS

similar to those that we have previously reported using diphenyl (DP) as organic crystal [7], or EBBA as liquid crystal [5]. Dispersed domains are constituted by an NP/PS solution that is rich in naphthalene. At room temperature NP was crystallized inside dispersed domains; therefore, dispersed domains scattered light and appeared opaque.

As it was expected, the domains size enlarges as the PS concentration in the blend increases. Heating above the NP melting point (81 ºC), rendered the films transparent (Figure 3).



(a) (b)

Figure 3. TOM micrographs for TRLS films synthesized using 55 wt % NP and 3 wt % PS obtained at: a) room temperature; b) 85 ºC

The phase diagram of the NP/PS binary system is shown in Figure 4. NP does not crystallize from PS rich solutions (up to the intersection between glass transition and melting curves at about 15 wt % NP). However, up to 30 wt % NP crystallization was not observed in the cooling cycle. For solutions with NP amounts greater than 30 wt % a partial crystallization of NP occurred during cooling as revealed by the location of glass transition temperatures measured in a subsequent heating scan. These glass transitions are located above the extrapolation of the glass transition vs. composition curve, but are significantly lower than the equilibrium value (located at about 310 K).

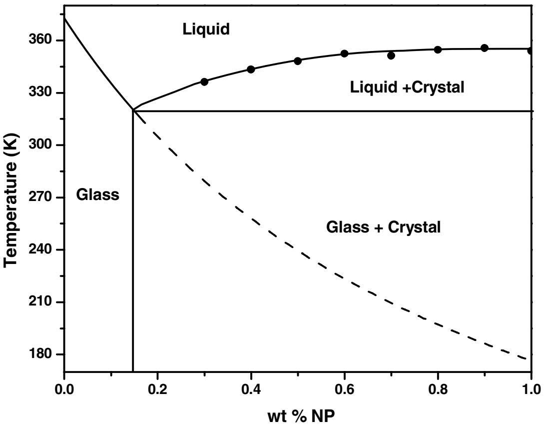


Figure 4. Phase diagram of the NP/PS binary blend

Figure 5 shows a DSC thermogram obtained for an NP/PS blend with 50 wt % NP. A crystallization peak is observed in the cooling cycle. In the subsequent heating devitrification of an NP/PS solution is followed by complex peaks that overlap melting and crystallization of NP, confirming that NP crystallization was not complete in the previous cooling cycle. The difficulty in producing complete crystallization of NP from its solution in PS constitutes an inconvenient to obtain reproducibility in the optical properties of TRLS films when different cooling and heating rates are employed.

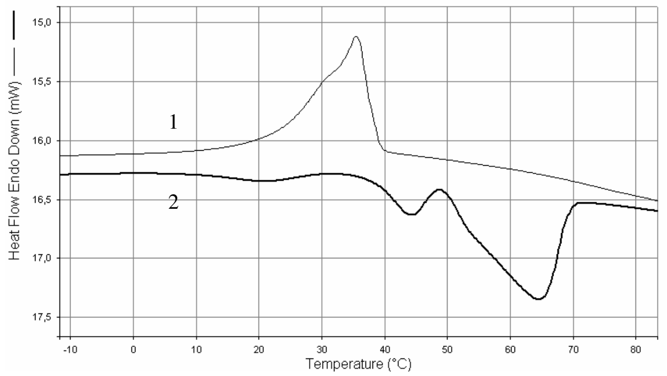


Figure 5. DSC thermograms of an NP/PS blend with 50 wt % NP: 1) cooling step, 2) heating step

Figure 6 shows the variation of the intensity of transmitted light as a function of temperature for a 200 μm-thickness TRLS film containing 55 wt % NP and 3 wt % PS. Successive heating/cooling cycles were performed at 5 °C/min. During a heating cycle NP crystallization took place in the 50 – 70 °C temperature range, increasing the fraction of crystals in dispersed domains and the opacity of the TRLS film (decrease in the intensity of transmitted light). Melting of NP crystals began at about 70 °C and was completed at 81 °C, producing a transparent TRLS film. In the following cooling cycle NP crystallization took place at about 48 °C leading to a very sharp decrease in the intensity of transmitted light.

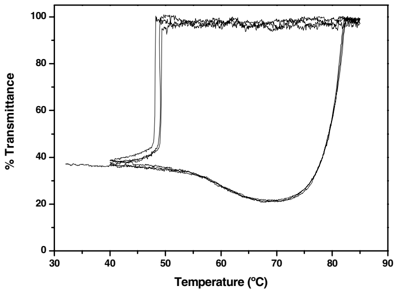


Figure 6. Intensity of transmitted light as a function of temperature in successive heating/cooling cycles, at 5 °C/min, for a 200 μm-thickness TRLS film containing 55 wt % NP and 3 wt % PS

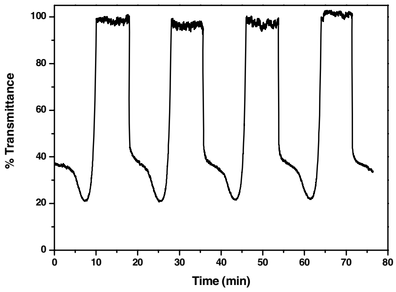


Figure 7. Intensity of transmitted light as a function of time in successive heating/cooling cycles, at 5 °C/min, for a 200 μm-thickness TRLS film containing 55 wt % NP and 3 wt % PS

This behaviour was quite reproducible for the selected rate of temperature change, as is shown in Figure 7 where variations in intensity during different heating/cooling cycles are plotted as a function of time.

The crystallization temperature certainly depends on the cooling rate but may also depend on the previous thermal cycle (e.g., in the case that a small fraction of crystals remains from the previous heating cycle it could induce a seeded crystallization at higher temperatures). Therefore, for TRLS films based on organic crystals (NP in the present case), the opaque to transparent transition temperature may be assessed, but the inverse transition (transparent to opaque) depends on the cooling rate and the thermal history of the material. This is a clear disadvantage of using organic crystals in TRLS films.

A different situation is observed when NP was replaced by a liquid crystal (EBBA) in the TRLS films synthesis [5, 6]. Figure 8 shows the intensity of transmitted light as a function of temperature during heating and cooling cycles at 2 ºC/min, for a 270 μm-thickness TRLS film containing 50 wt % EBBA and 1 wt % PS [5]. The thermal gap between transparent and opaque states is extremely reduced with respect to the case of using an organic crystal. A low undercooling (2 - 3 ºC) is enough to produce nematic domains inside dispersed particles. Evidently, the change in orientation of EBBA molecules that leads to a bidimensional array occurs much more rapidly than the organization of tridimensional organic crystals.

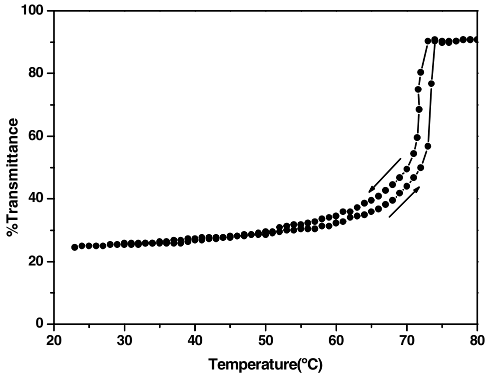


Figure 8. Intensity of transmitted light as a function of temperature during heating and cooling cycles at 2 ºC/min, for a 270 μm-thickness TRLS film containing 50 wt % EBBA and 1 wt % PS

Conclusions

TRLS films based on NP/PS domains dispersed in an epoxy matrix were synthesized in a single step by polymerization-induced phase separation. NP melting and crystallization were confined to the interior of dispersed domains leading, respectively, to transparent and opaque states. A major disadvantage of TRLS films based on organic crystals is the fact that a relatively large undercooling is necessary to produce a crystallization that occurs at a temperature that depends on the cooling rate and the thermal history. Therefore, the gap between transparent and opaque states is large and variable. These disadvantages are removed when the organic crystal is replaced by a liquid crystal. As nematic ordering occurs at a much faster rate than crystallization, the temperature gap between transparent and opaque states is significantly reduced in TRLS films based on liquid crystals.

Acknowledgements. The paper is dedicated to Professor Karel Dušek on the occasion of his 75th anniversary. The financial support of the following Argentine institutions is gratefully acknowledged: University of Mar del Plata, National Research Council (CONICET), National Agency for the Promotion of Science and Technology (ANPCyT), and Fundación Antorchas.

References

1. Dabisch W, Kuhn P, Muller S, Narayanan K (1980) DP 2907352
2. Hotta Y, Yamaoka T, Morohoshi K, Amano T, Tsutsui K (1995) Chem Mater 7:1793
3. Mucha M (2003) Prog Polym Sci. 28: 837
4. Millett F (2000) Brochure of Pleotint LLC www.pleotint.com
5. Hoppe CE, Galante MJ, Oyanguren PA, Williams RJJ (2004) Macromolecules 37: 5352
6. Hoppe CE, Galante MJ, Oyanguren PA, Williams RJJ (2004) Mater Sci Eng 24:591
7. Zucchi IA, Galante MJ, Williams RJJ paper submitted for publication