

Tailoring the Optical and Thermomechanical Properties of Polymer Host–Guest Systems

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ABSTRACT: For modern applications in microoptics, the refractive index (n) of polymers can be adjusted in a certain range by the addition of electron-rich organic dopants. As an unwanted side effect, a pronounced plasticizing occurs. In this work, the addition of a crosslinker (divinylbenzene) to an unsaturated polyester matrix, doped with phenanthrene for n adjustment, allowed us to successfully suppress the plasticizing effect measured after polymeriza-

tion. Even at high phenanthrene concentrations, the glass-transition temperature of the initial polymer could be almost retained. An increase of the polymer n from 1.5684 to a value of 1.6425 was achieved. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3514–3519, 2011

Key words: host–guest systems; glass transition; optics; polyesters; refractive index

INTRODUCTION

High-performance polymers with special optical and thermomechanical properties have gained more and more importance in different industrial applications and in consumer electronics, such as CD/DVD/Blu-Ray disk media, optical pickup systems, and plastic electronics.^{1–3} This has led to an increasing request for polymers with individually adjusted optical properties in combination with improved thermal stability to enable a higher continuous working temperature in comparison to the well-established poly(methyl methacrylate) (PMMA).⁴ The realization and commercialization of optical components made of polymers depend strongly on, among other things, the ease of processing and, finally, the suitability for mass production with low-cost replication methods. In the past, different molding techniques, such as UV embossing of curable polymer-based reactive resins, hot embossing, and injection molding, have been established.^{5–7} Only a few highly transparent plastic materials possessing a fixed refractive index (n) are commercially available; for certain applications, a modification of the optical properties, such as n , transmittance, and polarization, is desirable. In the case of curable reactive polymer resins, many different

(meth)acrylates, epoxides, and unsaturated polyesters are available that yield thermoplastic polymers or thermosets after polymerization. The optical transmittance in the visible range is around 90%, the n spans mainly a range from 1.49 (PMMA) to 1.56 (polycarbonate (PC), unsaturated polyesters, and epoxides).⁴

Depending on the aspired application, materials, for either the near infrared range, with classical telecommunication wavelengths between 1300 and 1600 nm, or the visible range between 380 and 780 nm for consumer electronics, have to be developed. Two main strategies can be pursued with respect to the n modification of polymers: First, a chemical synthesis of side-chain or block polymers enables a direct property tailoring.¹ Second, nanosized inorganic fillers or organic dopants are added to the polymer. Although the organics can be solved in the matrix up to the solubility limit, the inorganic material must be dispersed. As a rule of thumb, scattering and, hence, a loss of optical transmittance can be avoided only if the particles are smaller than a one-tenth of the investigated optical wavelength derived from Rayleigh's scattering law.⁸ Previous investigations have shown that the dispersion of commercially available nanosized ceramics, such as SiO₂, Al₂O₃, and ZrO₂, with primary particle sizes between 12 and 40 nm in polymers can only be used for small n changes because of particle agglomeration and, consequently, pronounced scattering at larger filler contents.^{9–11} The scattering depends strongly on the applied dispersion method because of the different deagglomeration forces of the used

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techniques.¹⁰ In case of very thin films in the micrometer range and according to the Lambert-Beers law for absorption, acceptable transmittance values, even at very high chemically modified nanofiller (ZrO_2 , TiO_2) loads up to 50 wt %, can be realized; hence, a pronounced n increase can be achieved.^{12,13} The *in situ* synthesis of organic-inorganic hybrid thin films exploiting the titania nanophase formation by the sol-gel reaction of titanium alkoxide in the presence of a polymer host enables large titania loads accompanied by a high n increase and good transmittance values for film thicknesses in the micrometer and submicrometer range.^{14,15} Transparent composites containing BaTiO_3 as a high- n filler were described in ref. ¹⁶. A comprehensive review on transparent-polymer-based nanocomposites can be found in ref. ¹⁷. A general overview of polymer-nanoparticle composites was published in 2010.¹⁸

The dissolution of electron-rich small organic molecules, such as phenanthrene and benzochinoline, containing a large number of π electrons in polymers increases n because of a pronounced molecular polarizability¹⁹ and enables, for example, polymer wave-guide fabrication or devices for free-space optics, such as lenses or prisms.²⁰ As an important drawback is that the addition of small organic molecules to the polymer matrix causes a pronounced plasticizing and a significant drop in the glass-transition temperature (T_g) range and prevents a commercial use.²⁰

In this contribution, the coeval influence of phenanthrene as an n modifier and divinylbenzene (DVB) as difunctional crosslinker on the polymer's optical and thermomechanical properties will be discussed.

EXPERIMENTAL

A commercially available unsaturated polyester-styrene resin (polymer content = 65 wt %, styrene content = 35 wt %, cobalt pretreated, Carl Roth Co., Karlsruhe, Germany) was used as a curable polymer matrix. The vendor did not supply any information about the chemical composition of the resin; earlier size exclusion chromatography experiments yielded an average molecular mass of around 1700 g/mol of the nonpolymerized resin as delivered.²¹ After solidification, the solid polymer possessed a T_g range of 80–90°C and good solubility in acetone and chloroform.²² Phenanthrene (Sigma Aldrich) was taken as received and added (0–40 wt %) with respect to n adjustment. DVB (Sigma Aldrich) was added (0–32 wt %) as a crosslinking agent. All components were mixed together with a high-speed stirrer (Ultraturrax T8, IKA) up to the solubility limit of phenanthrene, and the mixture was clear and highly transparent.

The host-guest mixtures were polymerized with the cold hardener curing agent methyl ethyl ketone peroxide (MEKP; supported by the resin vendor, composition: 25–35 wt % MEKP, 12.5–15 wt % 4-hydroxy-4-methyl-pentan-2-on, 3–5 wt % Butanon, and 3–5 wt % H_2O_2 ²²). According to the vendor's recommendations and reconfirmed in a different research work,²³ 3 wt % MEKP was added for mixture solidification under ambient conditions followed by a postcure at 80°C for at least 2 h to finish the polymerization. Under the given polymerization conditions, the addition of phenanthrene or DVB did not remarkably affect the polymerization reaction speed or the evolved polymerization heat. In comparison to styrene (boiling point = 145°, vapor pressure = 12.4 mmHg at 37.7°C). DVB possesses a higher boiling point and, therefore, a reduced vapor pressure (boiling point = 195°C, vapor pressure = 0.9 mmHg at 30°C; all data taken from product information at <http://www.sigmaaldrich.com>, accessed April 1, 2011). The evaporation of styrene or DVB during polymerization, due to released polymerization heat at the initial curing conditions under ambient conditions, was negligible. Increasing the DVB content reduced the solubility of the resulting copolymer in chloroform.

The viscosity of the uncured mixtures was measured with a cone and plate rheometer (Herrenberg, Germany) (Bohlin CVO50; 20°C, shear rate range = 1–200 1/s, 40 mm/4° cone, 150- μm gap); T_g (Mettler-Toledo FP900, equipped with a FP85 differential thermal analysis (DTA) cell, heating rate = 10°C/min) and the Vickers hardness (Paar-Physica MHT10) were measured after polymerization with a suitable test specimen. The n values of solid samples were characterized by an Abbe refractometer (Krüss AR2008, 589 nm, 20°C, experimental uncertainty = ± 0.0005). The optical transmittance of the solid specimen (sample thickness = 1.7–2.99 mm) in the 500–900-nm range was measured by a self-constructed optical equipment consisting of a halogen light source, a transmission unit with an integrating sphere (Ulbricht sphere), and a fiber optic microspectrometer. For better comparison, the optical transmittance data were normalized to a sample thickness of 1 mm by the application of Lambert-Beers law.

RESULTS AND DISCUSSION

Shear-rate-dependent viscosity of the uncured host-guest system

Because of plasticization, the addition of phenanthrene to the unsaturated polyester resin caused a pronounced viscosity drop. Figure 1 shows the shear-rate-dependent viscosity of the pure resin

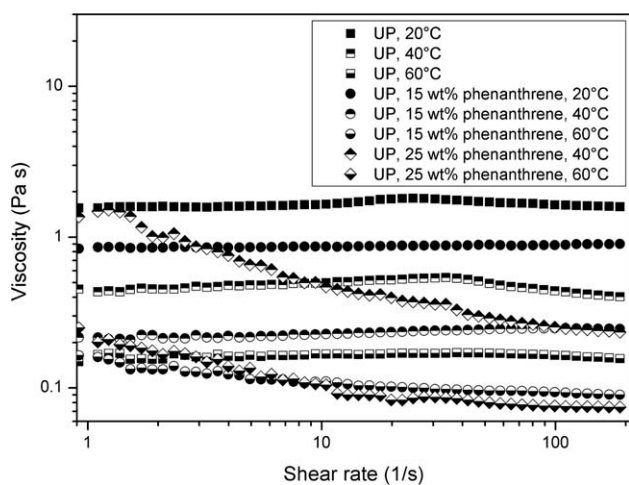


Figure 1 Change of the viscosity at different temperatures with the phenanthrene content.

unsaturated polyester (UP) and host-guest systems with 15 wt % phenanthrene at 20, 40, and 60°C; the mixture containing 25 wt % phenanthrene could only be measured at 40 and 60°C because, at 20°C, the host-guest systems solidified because of the precipitation of phenanthrene. The pure resin and the 15 wt % solution showed, at all investigated temperatures, an almost Newtonian flow with a pronounced plasticizing effect. In case of the mixture with 25 wt % phenanthrene load, the solubility limit was exceeded, the pseudoplastic flow behavior, especially at 40°C, gave evidence for the presence of a dispersion instead of a solution. A further temperature increase converted the dispersion again into a solution with further viscosity decay, especially at higher shear rates. The dilution of the unsaturated polyester resin with DVB caused a pronounced viscosity drop also. Figure 2 presents the shear-rate-dependent viscosity of solutions with 16 and 32 wt % DVB and, for better comparison, of the pure resin at

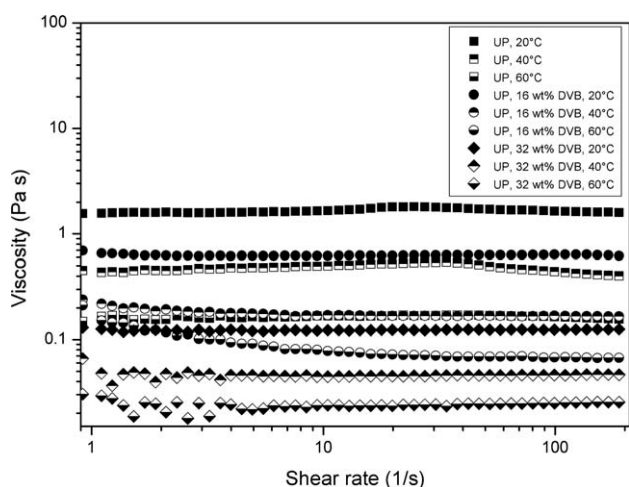


Figure 2 Change of the viscosity at different temperatures with the DVB content.

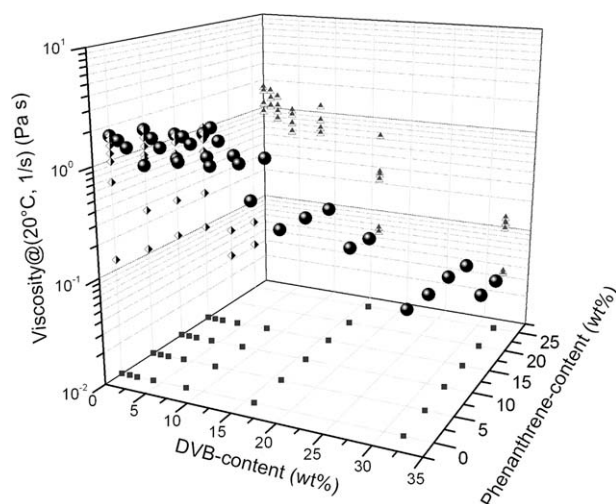


Figure 3 Change of the viscosity with the phenanthrene and DVB contents.

three different temperatures. Neglecting some scattering at 60°C and the low shear rates of the diluted mixtures again, we observed an almost Newtonian flow. The addition of both DVB and phenanthrene yielded a significant reduction of the mixtures' viscosity, which was favorable for device fabrication with the different reactive resin molding techniques. In Figure 3, the plasticizing and thinning effects of phenanthrene and DVB on the viscosity at 20°C (shaded balls) are given. For better understanding, the x - y projection (squares show the DVB and phenanthrene contents), x - z projection (semifilled triangles show the influence of the DVB content on the viscosity), and y - z projection (shown by semifilled diamonds) were added. Comparing the viscosity of the pure resin (1.639 Pa s, 20°C, shear rate = 100 1/s) with the mixture containing 25 wt % phenanthrene and 32 wt % (0.032 Pa s, 20°C, shear rate = 100 1/s), we achieved a significant viscosity reduction by a factor 51.

Optical properties: n adjustment and transmittance

As shown earlier, increasing the phenanthrene concentrations caused an almost linear increase of n .^{19,20,24} The addition of DVB should have caused a further rise of n because of the presence of easily polarizable electrons in the aromatic molecule. Figure 4 shows the change of n with the phenanthrene content at zero and a 32 wt % DVB amount. As a positive side effect, the solubility of phenanthrene was improved because of the presence of higher amounts of DVB. Unfortunately, with proceeding time (several months), an aging process, which means opacity of the test specimen, could be observed in the higher loaded mixtures. In general, a significant increase of n with the phenanthrene

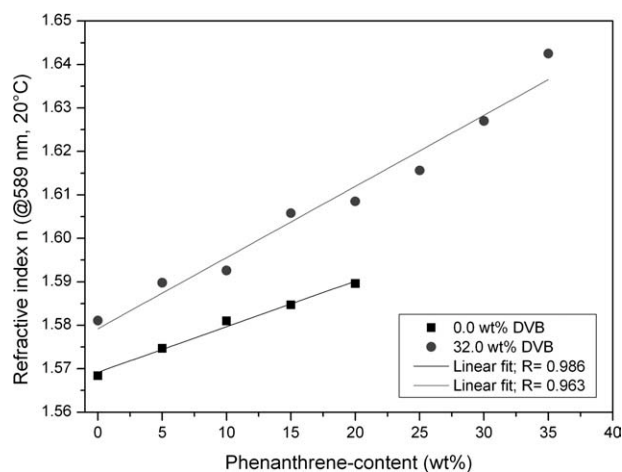


Figure 4 n changes with the phenanthrene content and different DVB concentrations.

concentration was seen. The slope of the curves was higher when DVB was present; quantitatively, the following fit equations (fit quality factor $R > 0.96$) for the n change could be used:

$$0 \text{ wt \% DVB : } n_{\text{mixture}} = 1.5692 + 1.05 \times 10^{-3} c_{\text{phenanthrene}} \quad (1)$$

$$32 \text{ wt \% DVB : } n_{\text{mixture}} = 1.5792 + 1.64 \times 10^{-3} c_{\text{phenanthrene}} \quad (2)$$

where n_{mixture} is the refractive index of the mixture and $c_{\text{phenanthrene}}$ is the phenanthrene concentration.

The fit equations were in good agreement with data obtained earlier for a series of organic chromophores, such as phenanthrene, benzochinoline, and 9-bromphenanthrene, solved in PMMA or unsaturated polyester.¹⁹ The obtained slope for the unsaturated polyester-phenanthrene mixtures differed slightly from the related one reported in ref.¹⁹ ($n = 1.5676 + 1.2 \times 10^{-3} \times c_{\text{phenan-}}$

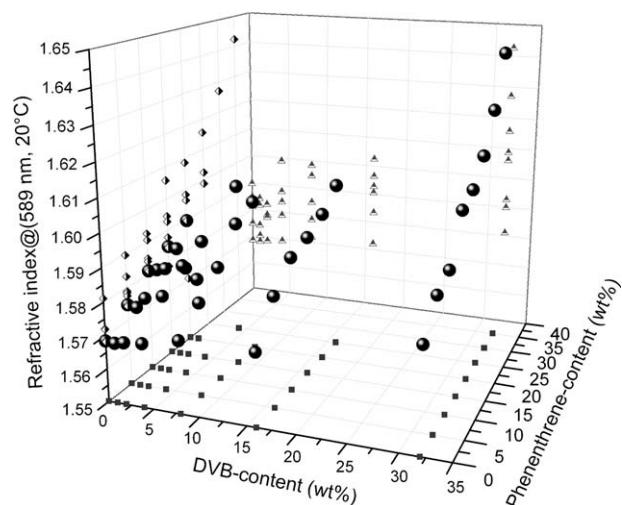


Figure 5 Change of n with the phenanthrene and DVB contents.

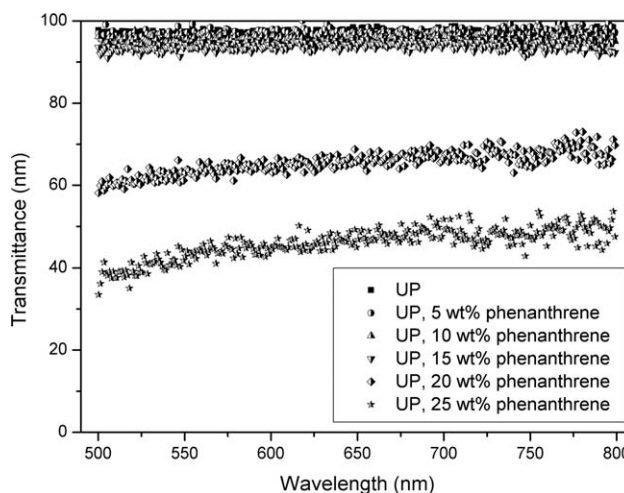


Figure 6 Optical transmittance of the mixtures containing phenanthrene.

threne), but this could be explained, on the one hand, by the experimental error of the n measurement and, on the other hand, by the fact that the composition of the commercially available unsaturated polyester reactive resin varied from batch to batch. DVB possessed a more extended, easily polarizable π -electron system than styrene²⁰; as a consequence, the refractive index of DVB ($n_D^{20} = 1.561$) was higher than that of styrene ($n_D^{20} = 1.546$, all data taken from product information at <http://www.sigmaaldrich.com>, accessed April 1, 2011). Therefore, it could be expected that increasing DVB amounts in the mixture would cause an increase of n . The larger slope of the DVB-containing mixtures may be explained by the formation of charge-transfer complexes between phenanthrene and DVB, which led to a further n increase. Figure 5 summarizes the impact of phenanthrene and DVB on n in all of the investigated mixtures (shaded balls). Again for better understanding, the x - y projection (squares show the DVB and phenanthrene content), x - z projection (semifilled triangles show the influence of the DVB content on the viscosity), and y - z projection (shown by semifilled diamonds) were added.

At a constant DVB concentration, the addition of phenanthrene caused a pronounced n increase; at a constant phenanthrene load, the addition of DVB led only to a small n increase. As a positive side effect, large DVB amounts (>16 wt %) increased the phenanthrene solubility up to 35 wt %, as demonstrated in Figure 5 for the highest DVB content of 32 wt %, which was accompanied by a high n of 1.6425 (Figs. 4 and 5). As described earlier, the higher loaded mixtures showed some aging, which resulted in a reduced optical transmittance. A further phenanthrene amount increase exceeded the solubility limit in the mixture's solid state, even in the case of freshly polymerized samples.

Figure 6 shows exemplarily the optical transmittance of the unsaturated polyester-phenanthrene

mixtures (data normalized to a sample thickness of 1 mm) in the range of 500–800 nm. The signal scattering was due to the applied measuring setup and the reduced plane parallelism of the solid test specimen. Up to a phenanthrene content of 15 wt %, the transmittance was only slightly reduced; the mixtures with 20 wt % and higher showed a pronounced transmittance decay, which could be attributed to the slow crystallization of the dye in the polymer matrix and the resulting opacity increase. At wavelengths below 500 nm, a pronounced yellowing and, hence, reduced optical transmittance were observed; these were in agreement with earlier observations.¹⁹ The yellowing could be attributed to the formation of charge-transfer complexes between different phenanthrene molecules; these complexes absorb in the range below 500 nm.

T_g

It was shown earlier that increasing amounts of inorganic nanoparticles or organic dopants cause a pronounced depression of the T_g because of the plasticizing of the resulting thermoplastic (PMMA) or thermoset (polyester) polymers.^{11,19,22} Figure 7 shows the influence of phenanthrene and DVB on the mixtures T_g after curing (shaded balls show the T_g of all systems, semifilled triangles show the projection T_g as function of the DVB content, semifilled diamonds show projection T_g as function of the phenanthrene amount, and squares show projection overview for all DVB and phenanthrene concentrations). At a constant DVB concentration, increasing phenanthrene amounts caused a pronounced T_g decay of the resulting thermoset polymer because of a pronounced plasticizing effect of the small molecule phenanthrene reducing the polymer chain–polymer chain interaction. Under ambient conditions, mixtures highly loaded with phenanthrene

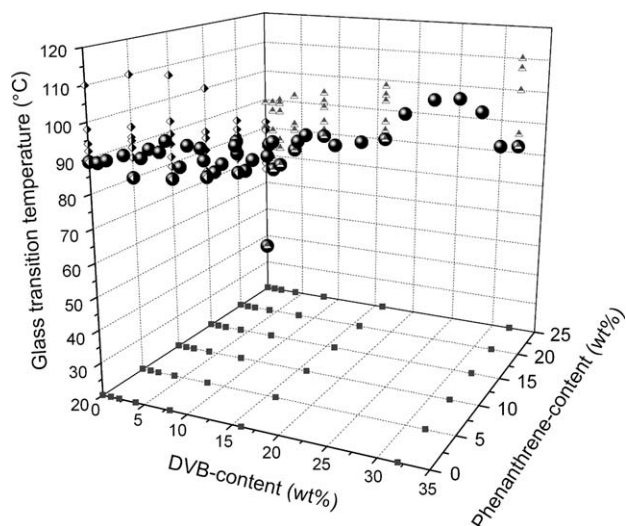


Figure 7 Change of T_g with the phenanthrene and DVB contents.

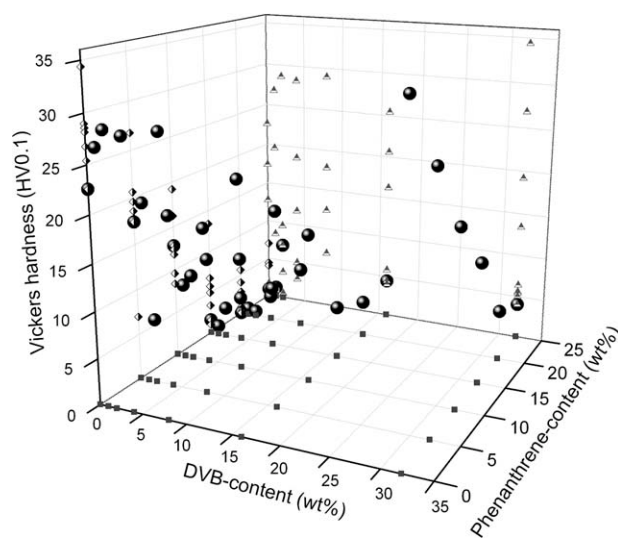


Figure 8 Change of the Vickers hardness with the phenanthrene and DVB contents.

behaved like a soft material and could not be used for technical purposes. At a constant phenanthrene load, ascending DVB concentrations led to a T_g gain because of an increasing crosslink density. Without any additive, the polymer possessed a T_g of 89°C; 32 wt % DVB addition enabled a slight T_g increase, up to 110°C. A mixture containing 25 wt % phenanthrene showed a T_g of 36°C; the addition of 32 wt % DVB yielded a T_g increase up to 82°C. All other investigated mixtures with intermediate dye and DVB amounts delivered intermediate T_g values. The given results show that in the final thermoset copolymer, the plasticizing effect of phenanthrene could almost be compensated by the copolymerization with DVB.

Vickers hardness

The measurement of the Vickers hardness of all systems partially confirmed the T_g results. In general, the addition of DVB elevated the mixture hardness, even at high phenanthrene concentrations; the addition of the dye yielded a pronounced hardness depression. Without dye presence, increasing DVB amounts raised the Vickers hardness from 22.6 (0 wt % DVB) up to a value of 34.4 (32 wt % DVB). At a phenanthrene amount of 25 wt %, an increase from 0.8 (0 wt % DVB) up a value of 4 (32 wt % DVB) was measured. The strong plasticizing effect of phenanthrene could not be completely compensated by increasing amounts of DVB. Figure 8 summarizes the measured Vickers hardness values for all investigated host–guest systems.

CONCLUSIONS AND OUTLOOK

The optical and thermomechanical properties of an unsaturated polyester matrix were significantly changed

by the addition of phenanthrene and DVB. Both molecules caused a pronounced lowering of the resulting host-guest mixture viscosity up to a factor of 50 in the uncured liquid state. n at 589 nm was significantly increased by both additives. The plasticizing effect of phenanthrene could be almost compensated by the difunctional DVB after polymerization, with the almost retention of T_g of the pristine polymer matrix. Pronounced plasticizing was also detected by the measurement of the mixtures' Vickers hardness.

With respect to thermoplastic device fabrication with adjusted n and good thermomechanical properties, the applied approach will be extended to methacrylates to enable the use of established casting and molding techniques.

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