

## Viscosity and Refractive Index Tailored Methacrylate-Based Polymers

Thomas Hanemann,<sup>1,2</sup> Kirsten Honnef<sup>2</sup>

<sup>1</sup>Karlsruhe Institute of Technology, Institute for Applied Materials-Materials Process Technology, Hermann-von Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

<sup>2</sup>Department of Microsystems Engineering, University of Freiburg, Georges-Koehler-Allee 102, D-79110 Freiburg, Germany  
Correspondence to: T. Hanemann (E-mail: thomas.hanemann@kit.edu)

**ABSTRACT:** With respect to the realization of new polymer optical devices with enhanced functionality there is a need for the development of new highly transparent polymer based systems with adjustable viscosity prior to curing and tailored refractive index as well as high continuous operation temperature after solidification. The use of phenanthrene as dopant enabled the increase of the refractive index in polymethylmethacrylate from 1.49 up to 1.55 (at 589 nm). A copolymerization of a dimethacrylate with the initial methacrylate/polymethylmethacrylate reactive resin suppressed the dopant-related plasticizing effect. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40194.

**KEYWORDS:** resins; optical properties; rheology; thermal properties; radical; polymerization

Received 12 August 2013; accepted 14 November 2013

**DOI:** 10.1002/app.40194

### INTRODUCTION

In recent years, optical components made of polymers gain more and more importance due to the possibility of using established shaping or replication methods, the reduced device weight in contrast to glass and the variety of commercially available polymers like polymethylmethacrylate (PMMA), polycarbonate (PC), or cycloolefinic copolymers (COC). In addition, there is an upcoming interest to use polymers as sensor materials, quite often in combination with optical waveguiding.<sup>1–9</sup> With respect to potential applications, different polymer properties have to be adjusted and controlled:

1. Optical transmittance (e.g., for waveguides)
2. Scattering, e.g., for OLEDs and organic solar cells<sup>10,11</sup>
3. Adjustable refractive index between 1.3 and 1.8
4. Continuous operation temperature
5. Thermal and chemical stabilities
6. Coefficient of thermal expansion
7. Rheological behavior (relevant for shaping and replication)

The first set of quantities (1–3.) are directly related to the aspired optical properties, the second set (4–7.) is related to side factors relevant during device application or, in case of the flow behavior, important during device fabrication. Interesting future polymer devices like large-scale 2D optical waveguide sensor arrays, evanescent field sensors, or Fiber Bragg gratings, need the development of polymers with individually adjusted optical as well as thermomechanical

and rheological properties beyond the related commercial ones.<sup>3,6</sup>

The successful realization and mass fabrication of polymer optical components depend among others strongly on the ease of processing and finally on the suitability for mass production using low-cost replication methods. In the last years, different molding techniques like UV-embossing of photocurable polymer-based reactive resins, hot embossing as well as injection molding have been established.<sup>5,7</sup> Future developments will focus more on direct fabrication techniques like inkjet printing or variants of nanoimprint lithography as well as reel-to-reel embossing and flexo or offset printing.<sup>6,12,13</sup> In these mentioned replication methods, UV-curable prepolymers (reactive resins, monomer-polymer mixtures) will play a prominent role due to their cold processing under ambient conditions and enhanced process control according to the chemistry of the UV polymerization process. At present different (meth)acrylates, epoxides, unsaturated polyesters and mixed variants like epoxy acrylates are commercially available. Depending on the chemical composition and the number of reactive centers in the molecule, thermoplastic polymers or thermosets will result after polymerization. The optical transmittance in the visible range (400–800 nm) is around 90%, the refractive index spans mainly a range from 1.49 (PMMA) up to 1.6 (PC, unsaturated polyesters, epoxides).<sup>3,14</sup>

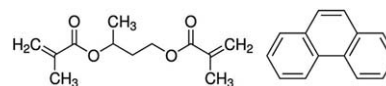
With respect to refractive index modification of polymers, two main strategies can be pursued: First, a chemical synthesis of

side chain or block polymers enables a direct property tailoring.<sup>1</sup> Second, nanosized inorganic fillers with large refractive index (titania, hafnium oxide, tantalum oxide) or organic dopants with extended delocalized  $\pi$ -electron system are added to the polymer forming polymer matrix composites (fillers) or host-guest systems.<sup>14–19</sup> The dispersion of nanosized ceramic fillers causes, due to particle agglomeration, pronounced scattering and hence significant optical losses.<sup>14–16,18,19</sup> Only an *in situ* synthesis of organic-inorganic hybrid polymers via the sol-gel route enables large titania loads accompanied by a significant refractive index increase and good transmittance values for film thicknesses in the micrometer and submicrometer range avoiding the presence of particles as scattering centers.<sup>5,20–24</sup> A comprehensive review about polymer nanocomposites for optical applications can be found in Szabó et al.<sup>14</sup>

In addition, polymers for special applications, e.g., polymer solar cells or OLEDs, have been developed in the past<sup>25,26</sup>; refractive indices more than 1.7 in the visible could be reached. Most of these polymers suffer from either huge synthetic effort or resulting high costs or a hindered processability using established shaping or replication methods.

In contrast, polymer host-organic guest mixtures contain electron rich small organic molecules like phenanthrene or benzochinoline possessing a large number of easy polarizable  $\pi$ -electrons, which increase the refractive index.<sup>17,27</sup> As a fundamental disadvantage the addition of these dopant molecules to the polymer matrix causes plasticizing and a pronounced reduction of the glass transition temperature range, demonstrated for unsaturated polyester-styrene and methylmethacrylate-polymethylmethacrylate (MMA/PMMA)-based polymer matrixes.<sup>17</sup> The small organic molecules, solved physically in the polymer matrix, extends the internal polymer chain distances, which cause an increase of the free volume. As a consequence the attractive interactions between different polymer chains are reduced. This causes the higher plasticity of the bulk polymer and reduces the glass transition temperature. To compensate the plasticizing effect the stiffness of the polymer matrix must be increased by a pronounced crosslinking applying polyfunctional monomers like diacrylates or triacrylates as comonomers. It was shown in previous work, that the addition of divinylstyrene as crosslinker to the host-guest mixture enabled a compensation of the plasticizing effect retaining almost the initial glass transition temperature of the pure solidified polymer matrix.<sup>27</sup>

In this work, the extension of this concept to methyl methacrylate-based systems was proved: First, the small molecule phenanthrene was selected as electron-rich organic dopant enabling a refractive index increase as shown in previous work.<sup>27,28</sup> 1,3-Butandiol dimethacrylate (BDMA) was chosen as difunctional crosslinker with a short aliphatic bridge between the reactive centers allowing for the formation of a more rigid polymer network. A suitable alternative to phenanthrene can be benzochinoline,<sup>17</sup> which is very costly. Instead of BDMA ethylene-glycol dimethylmethacrylate or bisphenol A dimethylmethacrylate could be used, the latter is also very costly (10 g approx. 50 €, Sigma Aldrich). It is expected that the combination of phenanthrene as dopant with a difunctional methacrylate as



**Figure 1.** Chemical structures of the used dopant phenanthrene and cross-linker 1,3-butandiol dimethacrylate (BDMA)

crosslinker and plasticizer antagonist a significant refractive index increase accompanied by an almost retain of the glass transition temperature range could be obtained.

## EXPERIMENTAL

A commercially available MMA-PMMA resin (polymer content: 30 wt %, trade name Plexit 55, Carl Roth company, Germany) was used as curable polymer matrix. In a first set of mixtures, the amount of BDMA (Sigma-Aldrich, Figure 1 left) as cross-linking comonomer was raised incrementally from 0 up to 4, 8, 16, and 32 wt %. These master host mixtures were individually doped with increasing phenanthrene (Sigma Aldrich, taken as received, Figure 1 right) amounts (0, 5, 10, 15, and 20 wt %). BDMA was added as crosslinking agent. All components were mixed together using a high-speed stirrer (Ultraturrax T8, IKA) up to the solubility limit of phenanthrene retaining a colorless and highly transparent mixture. All systems were polymerized thermally applying dilauroylperoxide (Sigma-Aldrich, further denoted as DLP, 1 wt % at 70°C for 24 h. In addition, the feasibility of UV polymerization was tested exemplarily applying 3 wt % photoinitiator D3358 (TCI Germany). To avoid adhesion on the glass substrate, a release agent (INT54, E. & P. Wuerz GmbH) was added to the reactive mixture. Table I shows the used sample series denotation in this work and the related effective composition of all investigated thermally cured mixtures considering all components including thermal initiator and release agent, Table II lists exemplarily the mixtures polymerized via UV curing.

The viscosity of the uncured mixtures were measured using a cone and plate rheometer (Bohlin CVO50; 20–60°C, shear rate range 1–200 1/s, 40 mm/4° cone; 150  $\mu$ m gap), the glass transition temperatures  $T_g$  via Differential Scanning Calorimetry (Netzsch, DSC204F1 Phoenix, heating rate 10°C/min) and the Vickers hardness (Paar-Physica MHT10) were measured after polymerization to suitable test specimen. The refractive indices of solid samples were characterized by an Abbe refractometer (589 nm, 20°C; Krüss AR2008, experimental uncertainty  $\pm 0.0005$ , 1-bromonaththalene as immersion oil). The optical absorbance of uncured liquid samples was measured applying a Cary 50 UV/Vis spectrophotometer (Varian) using disposable UV semimicro cuvettes (12.5  $\times$  12.5  $\times$  45 mm<sup>3</sup> outer dimensions, cuvette inner diameter 4 mm) in the 400–800 nm range.

## RESULTS AND DISCUSSION

### Flow Behavior of the Uncured Methacrylate Based Mixtures

With respect to processing and device fabrication, using inkjet printing, different relevant flow criteria were investigated in detail:

- Shear rate-dependent viscosity
- Influence of phenanthrene dopant concentration

**Table I.** Sample Series Denotation and Related Mixture Composition (in Round Figures to 100% Without Decimal Place)

Series denotation	Mixture composition (concentrations in wt %)				
	Plexit	BDMA	Phenanthrene	INT54	DLP
0 wt % BDMA series	98	0	0	1	1
	93	0	5	1	1
	88	0	10	1	1
	83	0	15	1	1
	78	0	20	1	1
4 wt % BDMA series	94	4	0	1	1
	89	4	5	1	1
	84	4	10	1	1
	80	3	15	1	1
	75	3	20	1	1
8 wt% BDMA series	90	8	0	1	1
	85	8	5	1	1
	81	7	10	1	1
	76	7	15	1	1
	72	6	20	1	1
16 wt % BDMA series	82	16	0	1	1
	78	15	5	1	1
	74	14	10	1	1
	69	14	15	1	1
	65	13	20	1	1
32 wt % BDMA series	66	32	0	1	1
	63	30	5	1	1
	59	29	10	1	1
	56	27	15	1	1
	53	25	20	1	1
48 wt % BDMA series	50	48	0	1	1
	48	45	5	1	1
	45	43	10	1	1
	43	40	15	1	1
	40	38	20	1	1

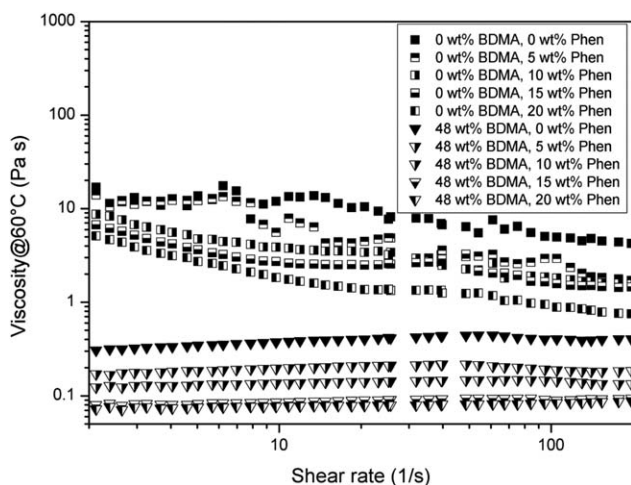
- Influence of BDMA crosslinker concentration
- Temperature influence on the viscosity

The pure Plexit/phenanthrene mixtures show in the investigated shear rate range of 1–200 1/s a pronounced pseudoplastic flow. Increasing phenanthrene content causes a viscosity drop due to

fostered plasticizing (Figure 2) and was observed in other reactive resin-dopant mixtures also.<sup>17,27</sup> The plasticizing effect is attributed to the reduced inner friction due to the separation of the polymer chains by the small guest molecules. Increasing amounts of the low-viscous BDMA (2 mPas@ [60°C, 100 1/s]) lowers the mixtures viscosity up to almost two decades, as a

**Table II.** Sample Series Denotation and Related Mixture Composition Used in UV Curing (in Round Figures to 100% Without Decimal Place)

Series denotation	Mixture composition (concentrations in wt%)				
	Plexit	BDMA	Phenanthrene	INT54	D3358
4 wt% BDMA series	92	4	0	1	3
	87	4	5	1	3
	83	3	10	1	3
	78	3	15	1	3
	74	3	19	1	3

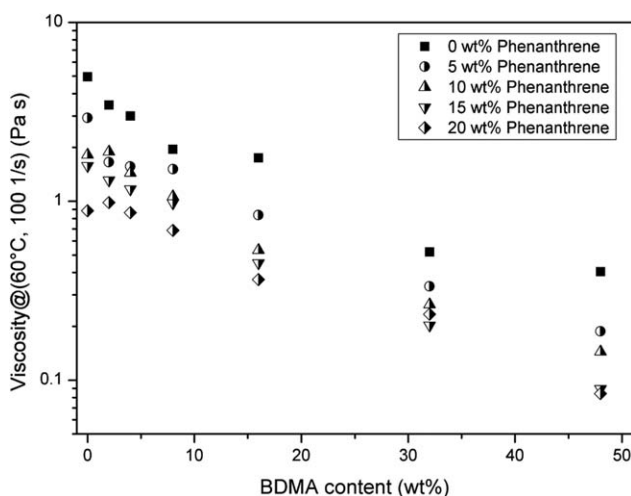


**Figure 2.** Shear rate dependent viscosities (at 60°C) as function of the BDMA and phenanthrene content

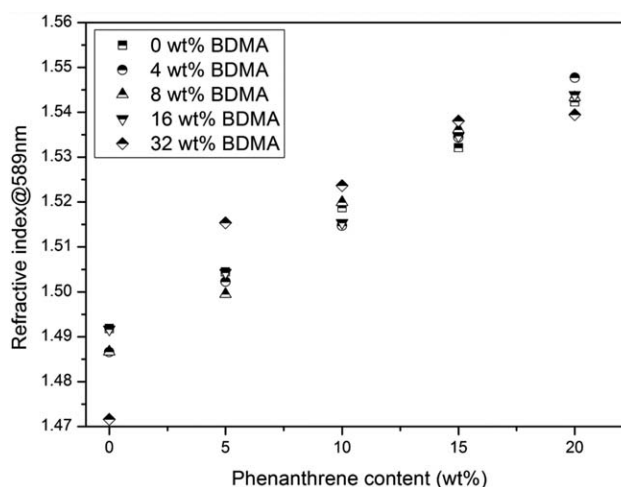
side effect the pseudoplastic flow is converted into an almost Newtonian one. This can be attributed to the reduced absolute polymer content and the accompanied polymer chain disentanglement during shear loading. Figure 3 shows, for a given temperature (60°C) and fixed shear rate, the impact of the dopant and crosslinker moiety on the mixtures viscosity. Both, phenanthrene and BDMA, yield a pronounced viscosity reduction, phenanthrene due to plasticizing, and BDMA due to the low viscosity of the pure monomer. By the variation of both molecules, the guest phenanthrene and the comonomer, the resin mixture's viscosity can be tailored due to the necessities of the applied replication method like inkjet or flexo-printing with subsequent UV-curing after shaping.

### Refractive Index Adjustment

As shown earlier the electron rich organic molecule phenanthrene can be used as suitable dopant for refractive index elevation of a polymer matrix system delivering an almost linear increase with concentration (Figure 4).<sup>17,27,28</sup> At constant phenanthrene content, the addition of BDMA causes a slight



**Figure 3.** Viscosity change (60°C, shear rate: 100 1/s) with BDMA and phenanthrene content



**Figure 4.** Refractive index gain with increasing phenanthrene and BDMA content

scattering of the refractive index values without showing a systematic correlation with concentration. Starting from initial pure solidified Plexit with a refractive index of 1.492@589 nm an increase up to a value of 1.548@589 nm (4 wt % BDMA, 20 wt % phenanthrene) could be achieved. Table III shows for all investigated systems the  $y$ -axis intercept  $n_0$ , the slope and the fit correlation parameter  $R^2$ . The estimated  $y$ -axis intercept value  $n_0$  are close together, same is valid for the resulting slope.<sup>17</sup> Higher BDMA concentrations do not change the slope, but cause a deterioration of the fit quality index value  $R^2$ .

In comparison to previous results, using a different MMA/PMMA composition prior to doping and curing a higher increase (slope) of the refractive index can be detected (for comparison<sup>17</sup>:  $n_0$ : 1.4938, slope: 0.0016, determined at 633 nm). Same is valid for a different host–guest system applying an unsaturated polyester–styrene resin matrix with phenanthrene as dopant (for comparison<sup>17</sup>:  $n_0$ : 1.5676, slope: 0.0012, determined at 633 nm, for comparison<sup>27</sup>:  $n_0$ : 1.5692, slope: 0.0011, determined at 589 nm).

In addition to thermal curing, exemplarily one mixture series (4 wt % BDMA, variable phenanthrene amount) were polymerized applying a homemade photoreactor consisting of a LED array (emission wavelength: 405 nm). The results in Table IV show

**Table III.** Increase of Refractive Index for All Investigated Systems (Variation of BDMA and Phenanthrene Content: Linear Fit Parameters)

Series (concentrations in wt%) variable	$n_0$ @589 nm	slope	$R^2$ -value
phenanthrene content			
0 BDMA	1.4922	0.0026	0.996
4 BDMA	1.4863	0.0030	0.995
8 BDMA	1.4872	0.0030	0.973
16 BDMA	1.4910	0.0027	0.986
32 BDMA	1.4859	0.0032	0.763
48 BDMA	1.4980	0.0032	0.901

**Table IV.** Refractive Index (@589 nm) Comparison of Thermally and UV-Cured Samples (photoinitiator 3 wt% D3358)

Mixture (concentrations in wt%)	$n_{\text{thermal}}$	$n_{\text{UV}}$
4 BDMA, 0 phenanthrene	1.487	1.495
4 BDMA, 5 phenanthrene	1.502	1.511
4 BDMA, 10 phenanthrene	1.515	1.520
4 BDMA, 15 phenanthrene	1.534	1.533
4 BDMA, 20 phenanthrene	1.548	1.545

that within the experimental error the refractive index values are almost identical irrespective of the selected solidification method.

Alternative methods to adjust the polymer matrix refractive index are based on the chemical modification of the polymer itself incorporating electron rich moieties. First, the methacrylate monomer can be modified containing e.g. an aromatic carbazole-phenoxy moiety.<sup>26</sup> Depending on the amount of the modified monomer in a PMMA-based copolymer a significant increase of the refractive index was measured. A copolymer containing 50 mol % of the modified methacrylate possesses a refractive index of 1.5876(@633 nm), the pure homopolymer shows a  $n$ -value of 1.6306(@633nm).<sup>26</sup> The synthetic effort of the modified monomer syntheses is quite high and hinders a widespread use. Second applying sol-gel methods enable the incorporation of organic-inorganic titanium moieties in the polymer network. Ho et al. investigated thin layers of a copolymer, consisting of an aromatic epoxy-derived monomer and organic titanium moiety, as suitable high refractive index material for optical circuits.<sup>29</sup> Depending on the film thickness and curing temperature, which causes a certain decomposition of the organic titania moiety, refractive index values around 1.77(@1550m, film thickness 1.6  $\mu\text{m}$ ) can be achieved. The optical transmittance at wavelengths higher than 600 nm is around 80–85%.<sup>29</sup> Epoxy based nanocomposites containing poly(glycidyl methacrylate) brush-grafted titania nanoparticles shows a refractive index around 1.62 (@633nm, 30 wt % titania load) but a reduced optical transmittance due the presence of nanosized particles.<sup>30</sup> Thin films of *in situ* generated titania nanoparticles in polyacrylic acid applying sol-gel technique shows similar values for the refractive index around 1.7 and a good transmittance around 90% (film thickness 200  $\mu\text{m}$ ).<sup>31</sup>

Quite recently, polymer nanocomposites containing ZnO or BaTiO<sub>3</sub> as high refractive index ceramic filler are under investigation.<sup>32,33</sup> Tao et al. investigated epoxy-ZnO nanocomposites for the application as LED encapsulation.<sup>32</sup> The measured average particle size is described to be around 4 nm. They found also a pronounced increase of the refractive index from 1.5(@633 nm) up to 1.65(@633 nm, 50 wt % ZnO). Despite the small particle size larger amounts of the filler cause a transmittance drop from 90% (neat epoxy) down to 80% (50 wt % ZnO).<sup>32</sup> Abe et al. described the fabrication of highly refractive BaTiO<sub>3</sub>-imidized poly(amic acid) nanocomposites.<sup>33</sup> The combination of the polymer with a huge amount of easy polarizable electrons and the high- $k$ -ceramic enables a refractive index of

1.88 (@635 nm) at a ceramic load of 50 vol %. Unfortunately, transmittance values were not presented.

All these latter listed materials—nanocomposites and special copolymers—suffer either from a complex synthetic effort prohibiting a larger amount of material or some restrictions in handling affecting device fabrication.

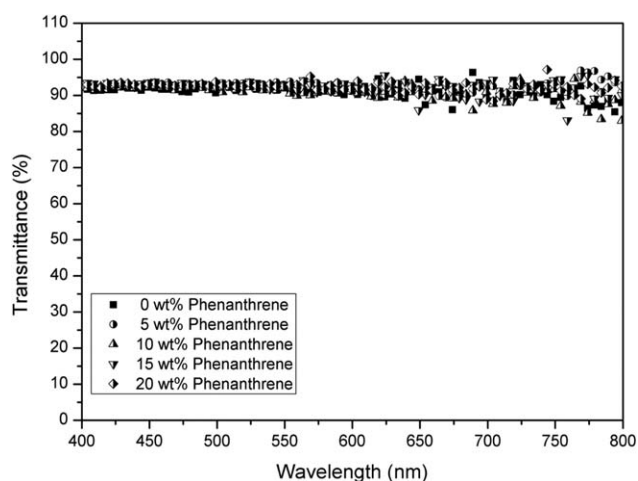
### Optical Absorbance

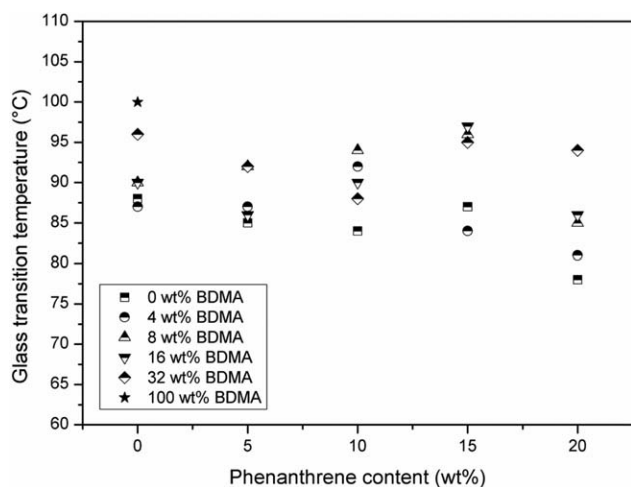
With respect to potential application as optical waveguides in the visible range it is important to investigate the influence of the crosslinker and the dopant on the absorbance properties. Figure 5 shows for the visible region (400–800 nm) the change of the optical transmittance with increasing phenanthrene and constant BDMA concentration (32 wt %) of the uncured mixtures prior to solidification. The addition of up to 20 wt % phenanthrene to the Plexit/BDMA mixtures does not change the optical transmittance. The results are in good agreement with earlier results covering mixtures containing up to 7.5 wt % phenanthrene in PMMA.<sup>17</sup> Increasing amounts of BDMA does not affect the transmittance due the lack of absorbing molecular moieties in the visible range. Earlier investigations on unsaturated polyester–styrene mixtures, doped with phenanthrene, showed a pronounced yellowing below 500 nm at higher dopant contents<sup>27</sup>, which may be attributed to the formation of charge-transfer complexes between the dopant and the aromatic moieties in styrene and the polyester matrix.

In contrast to composites containing metal oxide moieties described in the previous section<sup>29–32</sup> or special copolymer systems containing highly aromatic moieties,<sup>26</sup> which show a reduced transmittance in the whole visible range or a cut-off shift to higher wavelengths in the visible, the presented mixtures possess good transmittance values in the range from 400 to 800 nm around 90% close to commercial polymers enabling good signal transmittance.

### Thermomechanical Properties: Glass Transition Temperature

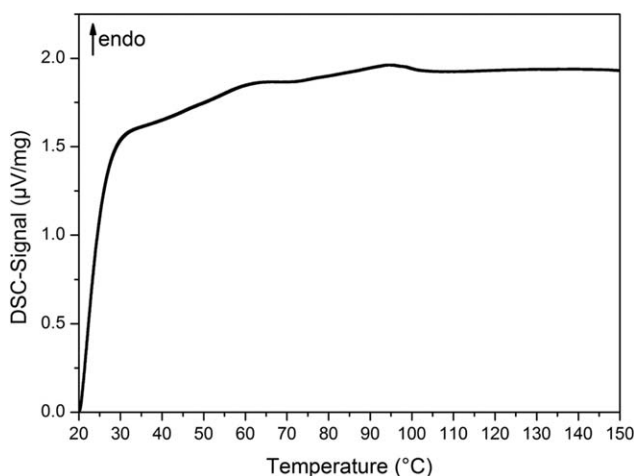
Previous results showed, that the addition of phenanthrene to a polymer matrix lowers the glass transition temperature  $T_g$  significantly in case of PMMA from 103°C down to 69°C at a

**Figure 5.** Transmittance in the visible range of a mixture containing 32 wt % BDMA and different concentrations of phenanthrene

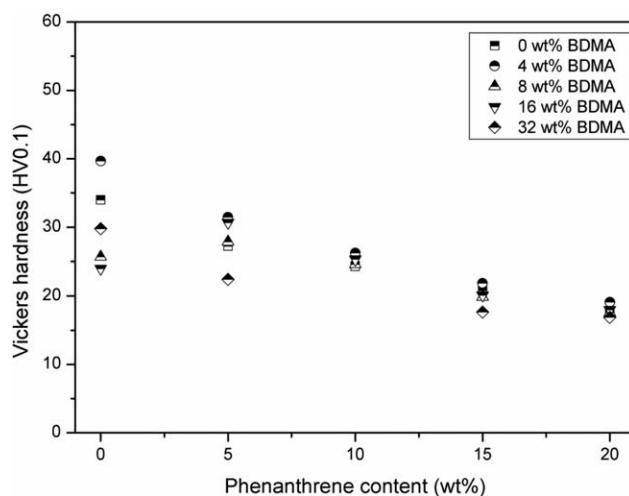


**Figure 6.** Change of the glass transition temperatures with phenanthrene and BDMA content

phenanthrene concentration of 20 wt % due to plasticizing.<sup>17</sup> Similar results can be found in the current investigation (from 88°C down to 78°C, see Figure 6). The numerical difference can be attributed to the experimental uncertainty and the evaluation of the DSC-measurement as well as of the polymers molecular weight distribution. Exemplarily one typical DSC-trace for the system 16 wt % BDMA, 20 wt % phenanthrene is shown in Figure 7. A very broad glass transition range starting around 75°C and ending around 95°C can be detected. It was also shown earlier, that the plasticizing effect can be partially compensated by the addition of crosslinker molecules.<sup>27</sup> An undoped cured polyester/styrene copolymer showed a  $T_g$  around 89°C, the addition of 25 wt % phenanthrene lowered  $T_g$  down to 36°C. A content of 32 wt % of the crosslinker divinylbenzene in the polymer matrix enabled a  $T_g$  raise up to 82°C, which is almost a compensation of the plasticizing. The addition of the difunctional BDMA to the initial resin composition counteracts successfully plasticizing. Figure 6 presents the measured  $T_g$  data for all investigated Plexit/BDMA/phenanthrene mixtures after ther-



**Figure 7.** DSC-trace of the system 16 wt % BDMA/20 wt % phenanthrene



**Figure 8.** Change of the Vickers hardness with phenanthrene and BDMA content

mal solidification as described earlier. Two main trends can be observed:

- Increasing phenanthrene content lowers  $T_g$
- Increasing BDMA content increases  $T_g$

With respect to the pure cured Plexit without any additive ( $T_g$ : 88°C) the polymer containing the highest amounts of phenanthrene and BDMA possesses a slightly increased  $T_g$  around 94°C, the plasticizing effect of phenanthrene can be compensated successfully. The total effect is small which is attributed to the  $T_g$  of pure poly-BDMA with a measured value around 100°C.

Polyfunctional (meth)acrylates are widely used in dentistry and orthodontics as curable resins enabling good mechanical stability in a broad temperature range which is accompanied by an elevated  $T_g$  due to the high crosslink density.<sup>34</sup> Complex highly crosslinked transparent acrylates and methacrylates have been synthesized by Bretterbauer et al. applying monomers with three (meth)acrylate moieties in one molecule for the realization of UV-curable coatings.<sup>35</sup> They describe systems with improved mechanical properties like scratch resistance and thermal stability up to 150°C due to the crosslinking process.

#### Vickers Hardness

The Vickers hardness results of all investigated systems deliver a principal softening irrespective if phenanthrene or BDMA were added (Figure 8). Especially at low phenanthrene contents no systematic influence of the BDMA amount on the sample hardness can be seen. At higher phenanthrene loads the BDMA amount becomes insignificant. In case of the earlier investigated polyester-styrene-DVB-phenanthrene mixtures the addition of the crosslinker caused a hardness increase.<sup>27</sup>

#### CONCLUSIONS

The rheological, optical and thermomechanical properties of a MMA/PMMA based reactive resin have been significantly changed by the addition of a dopant (phenanthrene) and a crosslinker (1,3-butyl dimethacrylate) prior and after thermal or

photochemical curing. Both additives cause a pronounced lowering of the mixture's viscosity up to a factor of 100 in the uncured liquid state. The refractive index at 589 nm is significantly increased by phenanthrene, from 1.49 up to approx. 1.55. The optical transmittance in the visible range is hardly affected by both additives. The pronounced plasticizing effect of phenanthrene, especially obvious in the drop of the glass transition temperature of the solidified samples, can be almost compensated by the difunctional crosslinker BDMA.

The results demonstrate the possibility to adjust the mixtures viscosity in a wide range suited to different shaping and replication techniques. The refractive index can be adapted easily in a wide band also by adding a dopant without affecting the transmittance behavior and with coval suppression of the typical plasticizing effect by copolymerization with a suitable crosslinker.

### ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support by Deutsche Forschungsgesellschaft (DFG) within the Collaborative Research Center "Transregio 123-Planar Optronics Systems." The authors thank Dr. M. Tosoni and O. Schwindt at KIT for the DSC measurements.

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