Synthesis and Characterization of Phosphorus-Containing Methacrylate-Based Difunctional Crosslinkers and Their Use In UV-Curable Resin Systems

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Two new phosphorus-containing methacrylate-based difunctional ABSTRACT: crosslinking agents [bis(4-(2-methacryloyloxy)ethyl carboxyl)phenyl phosphine oxide (BEPPPO) and bis(4-(2-methacryloyloxy)ethylcarbonylaminophenyl)phenyl phosphine oxide (BUPPPO)], which can be good candidates for UV-curable coating applications, were synthesized by reacting either a phosphorus-containing diisocyanate [bis(4-isocyanatophenyl)phenyl phosphine oxide] or a phosphorus-containing diacid chloride [bis(4-chloroformylphenyl)phenyl phosphine oxide] with hydroxyethyl methacrylate. The structures of the monomers thus obtained were characterized by FTIR, mass, and ¹H-NMR spectroscopies. The contents of the new crosslinking agents in the UV-cured polymeric films were varied between 10 and 30% by weight. Mechanical, physical, and thermal characterizations of the UV-cured films were investigated. An increase in crosslinking agent content caused an increse in mechanical properties. Films containing BUPPPO had higher tensile strength values compared to the films containing BEPPPO. Thermogravimetric analysis of phosphorus-containing crosslinking agents revealed that incorporating phosphorus into the structure resulted in a high char yield up to 24.5% at 600°C. Water absorption values of UV-cured films were also affected by the amount and type of crosslinking agent. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2575-2585, 1999

Key words: UV curable; phosphorus; methacrylate; crosslinking agents

INTRODUCTION

Radiation-curable coating applications have been continuously increasing because this technology combines advantages such as lower energy consumption, less environmental pollution, and very rapid curing even at ambient temperatures.^{1–3} UV-curable coating formulations generally consist of three major components: monofunctional or difunctional monomers, that are generally added to control the crosslinking density, as well as the viscosity; unsaturated oligomers; and photoinitiators. Additionally, nonreactive additives such as pigments, adhesion promoters, wetting agents, and so forth are also introduced into formulations to meet the specific application requirements.^{1–5}

Because of the increasing stringent safety regulations, the usage of fire resistant polymers has

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become compulsory for certain applications. To fulfill this requirement, halogen-containing compounds (as monomers or as additives) were widely used in the past. However, the evolution of hazardous toxic gases during combustion has been the major drawback for the further application of this approach. As an alternative, phosphorus-containing polymers have gained much attention in recent years. Phosphorus, when chemically bonded to the polymer structure, also brings a better solution for migration problems that were frequently observed for additive types of fire retardants.⁶

This work is a modified version of our previous effort that was focused on the synthesis of chemically bonded and hydrolytically stable phosphorus-containing monomers for the preparation of high performance polymers.⁷

In this work two new difunctional phosphoruscontaining monomers were synthesized that could also be potential candidates for use in the preparation of UV-curable resin compositions by reacting a phosphorus-containing diisocyanate [bis(4-isocyanatophenyl)phenyl phosphine oxide (BIPPPO)] or a phosphorous-containing acid chloride [bis(4-chloroformylphenyl)phenyl phosphine oxide (BAPPPO)] with hydroxyethyl methacrylate (HEMA). The resin used in this work was synthesized from isocyanatoethyl methacrylate (IEM) and polytetrahydrofuranediol (PTHF). Phosphorus-containing difunctional monomers were synthesized and introduced into the formulations changing from 10 to 30% by weight. The mechanical, physical, and thermal behavior of the polymeric films obtained via the UV-curing technique were investigated.

EXPERIMENTAL

Materials

The IEM (Dow Chemical Co.) was used without further purification. Purity was determined to be 99.3% according to the standard —NCO method.⁸ PTHF (BASF Inc.) was dried under a vacuum before use. Its hydroxyl number was determined to be 104 mg KOH/g.⁹ *N*-Vinyl-2-pyrrolidone (NVP, GAF Corp.) and diethyleneglycol diacrylate (DEGDA, Alcolac Int. Inc.) were dried over 4-Å molecular sieves before use. Tetrahydrofuran (THF) was dried over metallic sodium and distilled prior to use. Triethylamine (TEA, Fluka AG.), NaN₃, acetone, benzene, hydroquinone, SOCl₂ (Merck), MgSO₄(Aldrich), HEMA (Polyscience Inc.), isobutyl benzoinether (IBuBE, Stauffer Chemicals), and dibutyltin dilaurate (DBTDL, Merck) were used without further purification.

Characterizations

¹H-NMR, ¹³C-NMR, and ³¹P-NMR data were taken in DMSO-d₆ or in CDCl₃ using a Bruker AC 200 spectrometer operating at 200.132 MHz. FTIR spectra of the KBr disks or films of the samples were taken by a Nicolet-510P FTIR spectrometer. Mass spectra (MS) studies were performed at 70 eV with a Fision VG ZabSpec GC-MS. Glass transition temperatures were determined with a DuPont 910 differential scanning calorimeter (DSC). Scans were run at a heating rate of 10°C/min under nitrogen purge at a rate of 30 mL/min. Reported values were obtained from a second heating after a quick cooling. Thermogravimetric analysis (TGA) were performed on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min in air. A burning test¹⁰ was performed on the prepared films according to ASTM D-4804.

The gel content¹¹ of the UV-cured samples was determined by Soxhlet extraction for 12 h using an acetone-toluene mixture (1/1, v/v). The insoluble gel fraction was dried under a vacuum for 24 h at 60°C and was weighed to calculate the gel content.

Stress-strain measurements¹² of UV-cured free films were performed using an Instron tensile testing machine according to ASTM D 882-91. All stress-strain measurements were carried out uniaxially at ambient conditions.

Test samples were initially conditioned for 24 h at 50°C before immersing them in deionized water at 25 ± 0.5 °C for 24 h.¹³ The water absorption capacities of the cured samples were calculated from the weight differences between the dry films and those soaked in water.

Monomer Synthesis

Synthesis of BAPPPO

BAPPPO was prepared from its carboxylic acid according to the conventional procedure of acid chloride synthesis (Scheme 1).¹⁴

Synthesis of BIPPPO

A three-necked flask equipped with a mechanical stirrer and a thermometer was immersed in an

Sample	Ultimate Tensile Strength $(MPa) \pm 0.6$	Elongation at Break (%) ± 4	Water Absorption (wt %) \pm 0.1
68PTHFUMA/10DEGDA/20NVP/2IBuBE	3.0	19.0	8.8
68PTHFUMA/10BUPPPO/20NVP/2IBuBE	7.9	53.0	8.7
58PTHFUMA/20BUPPPO/20NVP/2IBuBE	6.8	50.0	8.9
48PTHFUMA/30BUPPPO/20NVP/2IBuBE	15.5	52.0	8.8

Table I Effects of BUPPPO Content on Tensile Properties of IEM/PTHF Based Polymeric Films

ice bath and charged with 4.49 g (0.0693 mol) of sodium azide in 20 mL of water.¹⁵ A mixture of 10 g (0.0247 mol) of acid chloride and 20 mL of acetone was then added from a separatory funnel to the vigorously stirred solution of the azide at such a rate that the temperature remained at 10-15°C. After the mixture had been stirred at this temperature for an additional 2 h, the layers were carefully separated. The upper organic layer was then added slowly to 200 mL of benzene that had been warmed to 60°C. A rather rapid evolution of nitrogen gas was observed and the mixture was kept at 60-70°C until nitrogen evolution ceased. The solution was filtered to remove any insoluble matter, and benzene was removed by distillation. The residue yielded 7.28 g (75%) of product. The product was characterized by the FTIR, ¹H-NMR, and mass spectroscopies (Scheme 2).

Synthesis of Crosslinking Agents

Synthesis of Bis(4-(2-Methacryloyloxy)ethylcarbonylaminophenyl)phenyl Phosphine Oxide (BUPPPO)

BIPPPO (13.96 g, 0.0384 mol) in THF was charged into a three-necked flask equipped with a stirrer, a dropping funnel, and a nitrogen inlet. DBTDL (0.08% by weight) was added into the reaction flask as the catalyst. HEMA (10.0 g, 0.0769 mol) was added slowly from a dropping funnel. After the addition was completed, the reaction mixture was stirred for a another 4 h at room temperature. The reaction was followed by the disappearance of the characteristic —NCO peak at 2261 cm⁻¹ in the FTIR spectrum. The yield of the product was 99% (13.0 g) and characterizations were made by FTIR, ¹H-NMR, and mass spectroscopies (Scheme 3).

Synthesis of Bis(4-(2-Methacryloyloxy)ethyl carboxyphenyl)phenyl Phosphine Oxide (BEPPPO)

HEMA (9.5 g, 0.15 mol), containing a trace amount of inhibitor (hydroquinone), was dissolved in 30 mL of dry THF and charged into a 250-mL three-necked flask equipped with a nitrogen inlet and a dropping funnel that was wrapped with aluminum foil to prevent adventitious polymerization. Then 20.2 g (0.05 mol) of acid chloride in 60 mL of dry THF was added dropwise to the reaction vessel at 25°C. The reaction mixture was stirred at room temperature for 5 h and a catalytic amount of Et₃N was added to complete the reaction. The mixture was stirred for a another 2 h and then the resultant triethylaminehydrochloride was removed by filtration and the filtrate was poured into 150 mL of distilled water. A waxy brown product was obtained. Unreacted HEMA and water soluble residual impurities were re-

Table II Effects of BEPPPO Content on Tensile Properties of IEM/PTHF Based Polymeric Films

Sample	Ultimate Tensile Strength $(MPa) \pm 0.6$	Elongation at Break (%) ± 4	Water Absorption $(wt \%) \pm 0.1$
68PTHFUMA/10DEGDA/20NVP/2IBuBE	3.0	19.0	8.8
68PTHFUMA/10BEPPPO/20NVP/2IBuBE	5.5	46.0	2.5
58PTHFUMA/20BEPPPO/20NVP/2IBuBE	5.0	40.0	5.0
48PTHFUMA/30BEPPPO/20NVP/2IBuBE	8.0	49.0	4.4

Table III DSC Results of Synthesized	
Crosslinking Agents BUPPPO,	
BEPPPO, and DEGDA	
	_

Sample	Glass Transition Temperature (T_g)
68PTHFUMA/10DEGDA/20NVP/	14
21BUBE 68PTHFUMA/10BUPPPO/ 20NVP/21BuBE	8
68PTHFUMA/10BEPPPO/20NVP/ 2IBuBE	3

moved from the crude product by washing at least 3 times with 150 mL of distilled water. The final product was dissolved in THF and dried with MgSO₄. The yield was 90% (\sim 26 g) after the evaporation of the THF. The product was kept under an N₂ atmosphere in a dark and cool place (Scheme 4).

Polymerization

Preparation of IEM/PTHF Prepolymer

PTHF (20.00 g, hydroxyl content 0.0396 mol) was charged into a flame-dried, three-necked, 250-mL

round-bottom flask equipped with a nitrogen inlet and a dropping funnel.⁷ DBTDL (0.08% by weight) was added into the reaction flask as the catalyst and the contents of the flask were stirred by a mechanical stirrer. The reaction temperature was kept between 15 and 20°C with a temperature controlled water bath. IEM (6.76 g, 0.0396 mol) was then added dropwise to the reaction mixture over a period of 1 h. The reaction was completed after 8 h. Completion of the reaction was monitored by the disappearance of the characteristic —NCO peak at 2261 cm⁻¹ in the FTIR spectrum.

Scheme 5 shows the reaction of IEM with PTHF in order to obtain PTHF urethane methacrylate (PTHFUMA) oligomer.

Preparation of Polymeric Free Films for Characterization

UV-curable acrylated urethane compositions were prepared by homogenously mixing PTH-FUMA oligomer with NVP as the reactive diluent, phosphorus-containing new crosslinking agents, and the photoinitiator (IBuBE). The amount of crosslinking agents was varied from 10 to 30 wt % and the photoinitiator (IBuBE) concentration was kept constant at 2 wt %, all on the basis of the final formulation. In order to



Scheme 2



obtain air bubble free films, the mixture was kept under moderately reduced pressure that did not upset the starting percentages of the components at room temperature for an appropriate time. Appoximately $200-\mu m$ thick polymeric films were prepared by pouring the viscous liquid formulations onto a TeflonTM coated mold. In order to obtain good flowability, the mixture, the mold, and the contents were heated to 35°C. In addition,

	Residue at 400°C (%)		
Composition	BEPPPO	BUPPPO	
68PTHFUMA/10DEGDA/20RD/2IBuBE	_		
68PTHFUMA/10CLA/20RD/2IBuBE	19.0	22.5	
58PTHFUMA/20CLA/20RD/2IBuBE	19.0	25.0	
48PTHFUMA/30CLA/20RD/2IBuBE	16.5	21.5	
98CLA/'IBuBE	37.5	30.5	
	Residue at 500°C (%)		
	BEPPPO	BUPPPO	
68PTHFUMA/10DEGDA/20RD/2IB11BE	_		
68PTHFUMA/10CLA/20RD/2IBuBE	6.0	10.0	
58PTHFUMA/20CLA/20RD/2IBuBE	11.0	12.5	
48PTHFUMA/30CLA/20RD/2IBuBE	9.0	6.5	
98CLA/IBuBE	28.5	26.0	
	Residue at 600°C (%)		
	BEPPPO	BUPPPO	
68PTHFUMA/10DEGDA/20RD/2IB11BE	0.5	0.5	
68PTHFUMA/10CLA/20RD/2IBuBE	2.0	3.5	
58PTHFUMA/20CLA/20RD/2IBuBE	4.5	5.5	
53PTHFUMA/30CLA/20RD/2IBuBE	5.5	5.5	
98CLA/IBuBE	24.5	20.0	

Table IVEffect of Crosslinking Agents (CLA) on ThermogravimetricAnalysis (TGA)



TEMPERATURE (°C)

Figure 1 TGA thermograms of films containing 10% crosslinking agents.

to prevent the inhibiting effect of oxygen, the resin in the mold was covered by a transparent 25- μ m thick TeflonTM film. Before irradiation with a high pressure UV lamp (OSRAM, 300 W), a quartz glass plate was placed over the TeflonTM film to obtain a smooth surface with the desired thickness. Finally, the formulation was irradiated for 210 s under a high pressure UV lamp. The

exposure time for adequate curing was previously determined in separate experiments by following the disappearance of the unsaturated methacrylate bands and gel contents of the films. For quantification of the extent of the polymerization, the 763 cm⁻¹ band due to the aromatic rings within IBuBE was used as an internal standard against the 810 cm⁻¹ band of unsaturation of methacrylate.

TEMPERATURE (°C)

Figure 2 TGA thermograms of 10-98% BUPPPO-based polymeric films.

RESULTS AND DISCUSSION

Synthesis of Phosphorus-Containing Diisocyanate

Scheme 1 and 2 show the synthesis routes of the phosphorus-containing diisocyanate BIPPPO. First the phosphorus-containing acid chloride BAPPPO was obtained, then the diisocyanate adduct was synthesized from BAPPPO and NaN₃. The chemical structures of the resulting compounds were characterized by FTIR, ¹H-NMR, and mass spectroscopies. The characteristic absorption peak of the functional group —NCO (2261 cm⁻¹) was detected for BIPPPO. Peaks at 1190 cm⁻¹(—P=O) and 1434–1437 cm⁻¹ (P—Ph)

TEMPERATURE (°C)

Figure 3 TGA thermograms of 10–98% BEPPPO-based polymeric films.

proved the existence of the phenyl phophine oxide structure. The compound was further characterized by ¹H-NMR. Absorptions of characteristic aromatic protons were found at δ = 7.4–7.6 ppm (C₆H₄—NCO) and δ = 8.15 ppm (P—C₆H₅). Moreover, from the MS the m/z was 359. Electron Impact (EI)-MS: m/z 359 (M⁺, 100%), 283 (M⁺—C₆H₅, 7%), 242 (M⁺—C₆H₅ —NCO, 17%), 226 (30%).

Synthesis of BAPPPO

BAPPPO was prepared by the conventional procedure of acid chloride and used directly.

Synthesis of Phosphorus-Containing Crosslinking Agents

Phosphorus-containing urethane methacrylate crosslinking agent (BUPPPO) was prepared by

the reaction of BIPPPO with HEMA as shown in Scheme 3. The reaction was monitored by FTIR. The disappearance of the absorption band at 2261 $\rm cm^{-1}$, which is assigned to the isocyanate group, is indicative of the completion of the reaction. Apparently, isocyanate and HEMA react by a nucleophilic attack by following a proton transfer. Therefore, the presence of an electron-withdrawing phosphine oxide group in BIPPPO reduces the electron density of the isocyanate carbon atom, thereby increasing the reactivity toward the alcohol.

The urethane acrylate that was synthesized was characterized by FTIR. Absorption bands at around 3400 cm⁻¹ (—N—H stretching), 1530 cm⁻¹ (—N—H deformation), and 1725 cm⁻¹ (—C=O) indicated the urethane structure. Other peaks at 1184 cm⁻¹(P—O—Ph), 1240 cm⁻¹

(P=O), and 1439 cm⁻¹ (P-Ph) confirmed the presence of phosphine oxide in the BIPPPO-based urethane acrylate ester. The ¹H-NMR spectra of urethane ester were consistent with its chemical structure. The multiplets associated with $(CH_2)_2$ ($\delta = 4.23-4.8$ ppm) protons confirmed that HEMA incorporated into the chain. Furthermore, the urethane structure was demonstrated by the singlet absorption of NH protons at $\delta = 5.49$ ppm. The absorption of aromatic protons were observed at $\delta = 7.4-7.7$ ppm. This observation suggests that triphenylphosphine was attached to the chain through BIPPPO. The singlets at $\delta = 1.88$ and 6.00 ppm arose from the CH₃ and (=CH₂) groups in the chain, respectively.

The other phosphorus-containing ester-based crosslinking agent, BEPPPO, was prepared by the reaction of acid chloride with HEMA as shown in

Scheme 4. The reaction was monitored by FTIR, ¹H-NMR, ¹³C-NMR, and ³¹P-NMR measurements: FTIR: 1720 cm^{-1} (s, aromatic and aliphatic carbonyls), 1640 cm⁻¹(m, C=C), 1520 cm⁻¹ (s), 1460 cm⁻¹ (s), 1100–1190 cm⁻¹ (s, C—O—C); ¹H-NMR $(CDCl_3): \delta = 8.15 \text{ (m, 4H)}, 7.4-7.6 \text{ (m, 9H)}, 6.15 \text{ (s, 6.15)}$ 2H), 5.6 (s, 2H), 4.64 (m, 4H), 4.50 (m, 4H), 1.95 (s, 6H); ¹³C-NMR (CDCl₃): $\delta = 167.09$ (Ar—C=O), 165.33 (acryl—C=O), 137.93 (C_{Ar}—P, substituted), 135.83 (C_{Ar}—P), 133.21 (C_{Ar}—C=O), 132.65 (C-ortho), 132.24 (C-meta), 131.88 (C-para), 129.77 (C-Ar, substituted), 128.98 (C-Ar, substituted), 126.20 (-C=), 120.83 (H₂C=), 63.17 (C ethylenic), 62.22 (C ethylenic), 18.23 (CH₃); $^{31}\mathrm{P}\text{-}\mathrm{NMR}$ (CDCl₃): $\delta = 28.6; \text{ MS} (70 \text{ eV}): 590 (M^+, 100\%), 461$ [M⁺-OCH₂OCOC(CH₃)CH₂, 52%], 341 (27%), 113 (79%, ethylmethylacrylate group), 69 (81%, methylacryloyl group).

Phosphorous-containing difunctional monomers were used in the UV-curable resin formulations as crosslinking agents at 10-30% by weight. Mechanical, physical, and thermal behaviors of polymeric films were determined. The mechanical and water absorption test results are given in Tables I and II.

Crosslinker structure and content have an affect on the properties of UV-cured polymeric free films. An increase in crosslinker content caused an increase in ultimate tensile strength in all of the films. Increasing the crosslinking agent increase the hard segment content and crosslinking density. The comparison of mechanical properties of BUPPPO- and BEPPPO-based crosslinkers showed differences in ultimate strengths. BUPPPO-based polymers showed higher tensile strength values then BEPPPO-based polymers. Generally, increasing the crosslinker content increases the ultimate strength. However, UV-cured polymeric films prepared from both crosslinking agents showed an unexpected behavior that could not be explained. An increase in the crosslinking agent content between 10 and 20% caused a decrease in the ultimate tensile strength values. This was prominent for BEPPPO. Similar behavior was also observed for the water absorption and tensile strength values. This effect was less pronounced for BUPPPO-containing formulations. This may be attributed to the fact that the decreasing urethane content, due to the decrease of PTHFUMA in the formulations, is replaced by the increasing amount of BUPPPO that also contains urethane groups that can form H bonding with water. An increase in the amount of absorbed water means more water will be trapped in the polymer network. Unpolymerized molecules

in the network lower the density of crosslinks and act as plasticizers, causing greater extensions prior to break. As the amount of absorbed water increases, the hydrogen bonding and dipole interactions between the chains are reduced. As the interactions mentioned above decrease, polymer chains gain greater mobility and therefore the elongation at break increases.

Crosslinking agents with different structures exhibit different thermal properties. The thermal properties of the crosslinking agents were investigated by TGA in air and by DSC in nitrogen; the results are given in Tables III and IV. TGA plots of formulations that contain phosphorus-containing crosslinking agents provide additional information in regard to their thermal stability.

CONCLUSION

Two new phosphorus-containing and methacrylate-based unsaturation difunctional UV-curable crosslinking agents, BUPPPO and BEPPPO, were synthesized. The chemical structures of the monomers were characterized by FTIR, mass, and ¹H-NMR spectroscopies. UV-curable resin films were prepared by the introduction of the phosphorus-containing new crosslinking agents into the formulations, changing from 10 to 30% by weight. The mechanical, physical, and thermal behavior of UV-cured free films were determined. An increase in the weight percent of crosslinker caused an increase in mechanical properties. BUPPPO-containing formulations displayed better mechanical properties than BEPPPO-containing ones. The water absorption values of polymeric films containing BUPPPO were higher than those with BEPPPO. It is well known that urethane groups form strong hydrogen bonds with water molecules. Therefore, the higher water absorption values of the above-mentioned polymeric films may be explained by the additional urethane groups that were introduced into the formulations by BUPPPO. The thermal analysis of phosphorus-containing crosslinking agents revealed that incorporation of phosphorus into the polymers can increase the char yield up to 24.5% at 600°C if the polymeric films were prepared from neat crosslinking agents. TGA results of the char yield at 400, 500, and 600°C are given in Table IV and in Figures 1–3. Introduction of even 30% crosslinking agents, which have considerably high molecular weight, into the formulations can

only contribute a small amount of phosphorus into the whole system. As a result, the char yields of the polymeric films containing 10-30% crosslinking agents had lower char yield values compared to the films prepared from pure crosslinker. However, as can be seen from the TGA plots, films prepared from phosphorus-containing crosslinking agents showed higher char yields at 600°C (3.5% for BUPPPO and 2% for BEPPPO) than the films prepared from the non-phosphorus-containing crosslinking agent DEGDA, which can only yielded 0.5% char.

A burning test¹⁰ was conducted with $100 \times 10 \times 0.02$ mm samples; 75 mm of polymer films containing 1.56 and 1.50% phosphorus for BEP-PPO and BUPPPO burned in 52 and 50 s, respectively. The average burning time of non-phosphorus-containing samples (DEGDA) was 32 s. Additionally, phosphorus-containing films left a visible amount of char compared to the DEGDA-containing films.

The low T_g of BUPPPO- and BEPPPO-based polymers can be explained by the more flexible structure and higher molecular weights of the PTHFUMA-based oligomer.

For all formulations the gel contents were found to be higher than 95%.

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