

Synthesis of Poly(propylene-Glycol-Diacrylates) and Properties of the Photocured Networks

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ABSTRACT: A series of poly(propylene-glycol-diacrylates) (PPGDA) having molecular weights (MW) in the range 300–3,000 and an acrylic functionality near to two were synthesized by acrylation of the corresponding hydroxy-terminated oligomers with acrylic acid in the presence of *p*-toluensulphonic acid as a catalyst. The \bar{M}_n of the acrylated products was found slightly lower than that of the starting oligomers, indicating the occurrence of an acidic degradation reaction which does not influence the acrylic functionality. The acrylated oligomers were ultraviolet (UV) cured until a complete double bond disappearance was obtained: only in the presence of tripropylene-glycol-diacrylate (TPGDA) were small amounts of residual unsaturations revealed. Rubbery materials were usually obtained, with the exception of TPGDA. The properties of the cured PPGDA were investigated by means of differential scanning calorimetry, thermomechanical analysis, and dynamic mechanical thermal analysis. The T_g values were found to decrease by increasing the MW of the used oligomers, that is, by increasing the length of the chain between the two acrylic double bonds. A good agreement with the Nielsen equation was found. Moreover, the equilibrium swelling values in water were measured; the obtained values were interpreted in terms of the solubility parameters of the oligomers and of the crosslinking density of the networks. Finally, some mixtures of PPGDA oligomers with a typical epoxy-acrylate resin were UV cured; their properties confirm the high flexibilizing effect of the PPGDA oligomers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 491–497, 1997

Key words: UV curing; poly(propylene-glycol-diacrylates); networks; epoxy-acrylate resin

INTRODUCTION

In previous articles, we studied the properties of polymeric films obtained from ultraviolet (UV)-cured poly(ethylene-glycol-diacrylates) (PEGDA)¹ and poly(tetramethylene-ether-diacrylates) (PTMEGDA),² investigating the structure-property relationships for the different series of oligo-

mers. The examined parameters concerned the repeating unit composition, the molecular weight (MW) of the oligomer, and its acrylic functionality.

Pursuing this research, we have taken into account poly(propylene-glycol-diacrylate) (PPGDA) oligomers. They were obtained from the corresponding *bis*-OH-terminated products having different MW in the range 300–3,000.

The interest in using these products is connected with the high flexibility of the poly(propylene-glycol) (PPG) structure, good polarity and solubility properties, good stability, and hydrolysis resistance, as reported in the literature.^{3,4} These

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properties explain the wide use of PPG as intermediates in polyurethane synthesis and the production of lubricants and surface active agents.

Some PPGDA products such as tripropylene-glycol-diacrylate (TPGDA) are well known and are currently used as reactive diluents in commercial UV-curable formulations.^{5,6} A systematic study of the change of the properties of these oligomers as a function of the MW has not yet been reported.

In this work, we studied the preparation and characterization of PPGDA oligomers, their photopolymerization, and the properties of the networks formed after the curing reaction. Some preliminary results on these systems were reported elsewhere.⁷ Moreover, mixtures of the PPGDA oligomers with a typical epoxy-acrylic resin were examined in order to evaluate the flexibilizing properties of these oligomers introduced in a rigid network.

EXPERIMENTAL

Materials

Solvents and reagents (Fluka) were distilled before use and stored under dry N₂. TPGDA was an Aldrich product; it was used as received. PPGDA 400 oligomer was prepared by acrylation of the corresponding di-hydroxy-PPG oligomer (Fluka); the other PPGDA oligomers were prepared by acrylation of the corresponding di-hydroxy-PPG oligomers, supplied by Aldrich (see below).

As a typical epoxy-acrylate resin, *bis*-phenol-A-diglycidyl-ether-diacrylate (BGEA), having an epoxy equivalent of 195, was used; it was kindly supplied by UCB Belgium (Ebecryl 600). Benzyl-dimethyl-ketal (Ciba-Geigy) was used as a photoinitiator at 4 wt % concentration.

Synthesis of PPGDA oligomers

The preparation of PPGDA 725 is reported in detail. The other oligomers were prepared according to the same procedure. Ten grams of PPG 725 (Aldrich) were dissolved in benzene (80 cm³), 50 mg of hydroquinone and 2.7 cm³ of acrylic acid (30% stoichiometric excess) were added, and the mixture was refluxed for 2 h in a glass flask equipped with a Markusson head. Subsequently, 0.5 g of *p*-toluensulfonic acid was added and the mixture was refluxed for 9 h at about 130°C with

azeotropic distillation of water. The reaction mixture was treated with K₂CO₃, in order to eliminate catalyst and free acrylic acid, stirred for 2 h at 40°C, and filtered. Then, the solvent was evaporated in a Rotovap evaporator under vacuum. The final product (10.7 g) was obtained and had an acrylic functionality of 1.94 and an acid number of 0.56 (number of milligrams of KOH required to neutralize 1 g of sample). We named the acrylated products with a code indicating their chemical structure, followed by a number denoting the MW of the *bis*-OH-terminated oligomer used for preparing the diacrylated compound.

Curing Procedure

The mixtures of the pure acrylated oligomers with 4% (w/w) of the photoinitiator were coated onto glass plates with a calibrated wire-wound applicator to obtain a film thickness of about 100 μm. Coated sheets were then irradiated with a medium-pressure mercury lamp with a light intensity on the film of about 8 mW/cm², in a small box equipped with a quartz window under pure N₂ atmosphere (O₂ content < 20 ppm).

Free films were obtained by peeling them from the glass plate and completing the curing process by irradiating the other side of the film. The irradiation time was continued until a constant double bond conversion was reached (about 20 sec). The complete procedure was reported previously.¹

Analyses and Film Characterization

Fourier transform infrared (FTIR) analysis was performed on the products coated on a KBr disk before and after UV curing, by means of a Mattson Genesis spectrometer. Acrylic functionality was determined through the saponification method by using an alcoholic KOH solution according to the reported procedure.⁸ Viscosity measurements were performed with a Contraves Rheomat 15 viscometer at 25°C. \bar{M}_n determinations were carried out with a Gonotec Osmomat 070-SA in CHCl₃ solution at 37°C with benzil calibration. Gel permeation chromatography (GPC) was performed on a Varian 5020 Instrument, in THF solutions at 25°C with two Styragel columns (Polymer Laboratories) having 50 and 100 Å pore size and a refractive index detector. Calibration was performed with polystyrene standards. Film thickness was measured with a Minitest 3000 instrument (Elektrophysik Köln, Germany).

Table I Properties of PPGDA Oligomers

Oligomer	\bar{M}_n^a	\bar{M}_n^b	Acrylic Functionality	Viscosity at 25°C (cP)	Acid Number ^c
TPGDA		300	1.83	7.9	2.03
PPGDA 400	445	393	1.98	16.9	0.68
PPGDA 725	727	830	1.94	24.9	0.56
PPGDA 1000	995	1,063	2.0	33.8	0.8
PPGDA 2000	2,085	1,619	1.95	141.2	0.7
PPGDA 4000	2,942	2,691	1.75	605.8	0.98

^a PPG oligomer used.

^b Oligomer after acrylation.

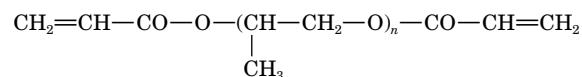
^c Number of milligrams of KOH required to neutralize 1 g of sample.

Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 20 instrument; thermomechanical analysis (TMA) was performed on a Mettler TMA 40 instrument, equipped with a low-temperature probe. Dynamic mechanical thermal analysis (DMTA) was carried out on a Polymer Laboratories Instrument MK II at 5-Hz frequency in the tensile configuration. E_1 and $\tan \delta$ were measured as a function of temperature. The size of the specimen strips was about $20 \times 40 \times 0.1$ mm. Swelling values in water were obtained as the ratio of the final volume to the initial volume of the sample after 16 h of water treatment. Gel contents were determined by measuring the weight decrease after a 16-h treatment with CHCl_3 .

RESULTS AND DISCUSSION

Properties of Pure PPGDA Oligomers

The structure of PPGDA oligomers can be schematized as follows:



where n ranges from 3 to about 47. In Table I, some characteristics of the different PPGDA oligomers used are reported. All of the oligomers are liquid at room temperature, with viscosity values clearly lower with respect to PEGDA¹ and PTMEGDA² oligomers. The —OH functionality was very near to two, as evaluated on the basis of their hydroxyl number. Therefore, for the oligo-

mers used, the presence of allylic terminal unsaturations, as suggested in the literature,⁴ is to be considered very limited.

By comparing PPGDA with the corresponding PPG products, a decrease of the \bar{M}_n values is observed, which is more evident by increasing the MW of the oligomers. At the same time, the acrylic functionality remains practically constant and near to two double bonds per molecule. The same behavior was observed in the synthesis of PTMEGDA and was attributed to a hydrolytic attack on the oligomer chain by the acidic catalyst in the presence of water with the formation of hydroxy groups; they are then subjected to the acrylation reaction.² It can be noted that the acidic degradation is less evident with respect to PTMEGDA oligomers. In Figure 1, the GPC chromatograms of PPGDA 2000 before and after the acrylation reaction are reported; they confirm the decrease of the MW of PPGDA.

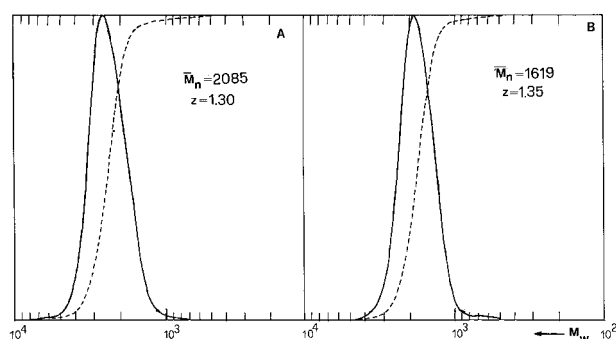


Figure 1 GPC traces of (A) PPG 2000 and (B) the corresponding acrylated product.

Table II Properties of UV-Cured PPGDA Oligomers

Oligomer	d.b. conv. (%)	Gel Content (%) ^a	T_g^b (°C)	T_g^c (°C)	T_g^d (°C)	Swelling % ^e
TPGDA	93.0	96.3	27.8	30.0	58.8	0
PPGDA 400	100	96.4	-24.7	-21.5	-7.1	2.05
PPGDA 725	100	97.7	-49.8	-48.1		6.62
PPGDA 1000	100	96.9	-60.4	-60.8	-36.2	8.85
PPGDA 2000	100	97.3	-65.1	-61.7	-43.5	13.30
PPGDA 4000	100	90.8	-69.9	-76.2	-47.7	15.50

^a Determined by CHCl_3 treatment.

^b By DSC.

^c By TMA.

^d By DMTA.

^e In water at 25°C.

Properties of UV-Cured PPGDA Oligomers

In Table II, some properties of the pure UV-cured PPGDA oligomers are reported. The double bond conversion was calculated by means of FTIR analysis, comparing the spectra of the oligomer before and after the curing process. A complete double bond conversion for all of the oligomers with the exception of TPGDA was found, considering the double bond signals at 1,635 and 1,620 cm^{-1} . As an example, the spectrum related to PPGDA 1000 is reported in Figure 2.

In the case of TPGDA, the conversion is not complete. This fact can be attributed to the high crosslinking density of the network, which decreases the mobility of the reactive species (vitrification).⁹ Moreover, the gel content was practically complete for all of the oligomers, indicating that all of the molecules are linked to the network. Only PPGDA 4000 shows lower gel content value, in agreement with its lower acrylic functionality.

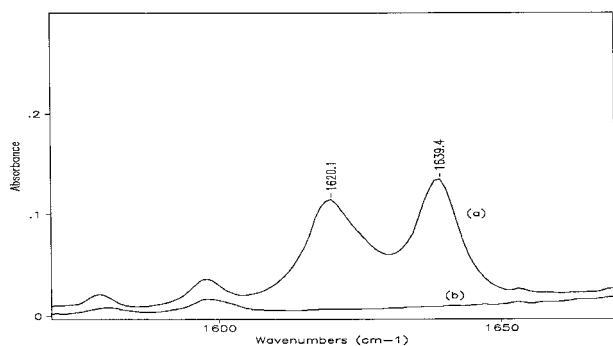


Figure 2 FTIR spectra of PPGDA 1000 film (A) before and (B) after UV irradiation.

DSC, TMA, and DMTA of the cured oligomers indicate that rubbery products are obtained, with T_g values decreasing by increasing the oligomer MW. A typical DSC thermogram related to a UV-cured PPGDA 400 film is plotted in Figure 3, while in Figure 4, a TMA pattern of a UV-cured PPGDA 2000 film is reported.

In Figure 5, a DMTA spectrum related to a UV-cured PPGDA 1000 film is reported. It can be seen that $\tan \delta$ reaches its maximum value at about -36°C , which can be considered as the T_g of the material. In the same temperature interval, the storage modulus E_1 shows a sharp decrease, confirming the occurrence of the glass transition.

By considering the T_g values obtained by means of DSC, TMA, and DMTA (Table II), it can be noted that DSC and TMA results are very similar, whereas those from DMTA are shifted toward higher values. Similar behavior was observed for

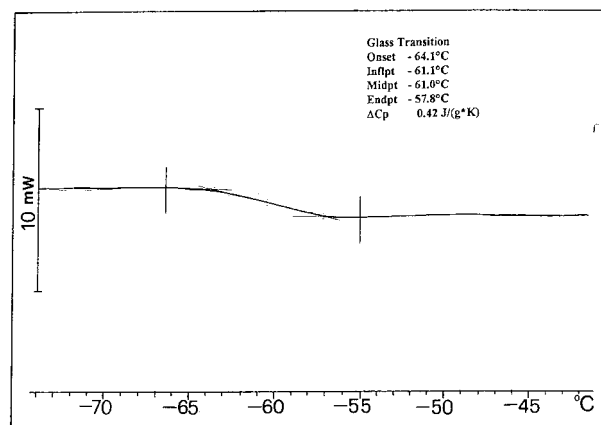


Figure 3 DSC thermogram of UV-cured PPGDA 400.

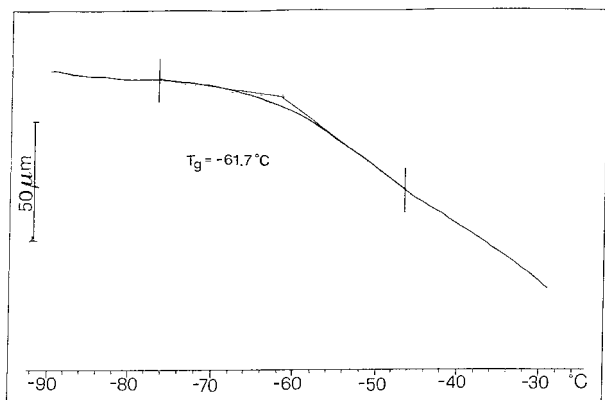


Figure 4 TMA thermogram of UV-cured PPGDA 2000 film.

PEGDA and PTMEGDA oligomers^{1,2} and was attributed to a frequency effect.^{10,11}

Network Characterization

It is well known that the T_g value increases by increasing the network crosslinking density. Relationships were proposed for this dependence by Nielsen.¹⁰ If the mobility of the system is not much changed by introducing the acrylic double bond, we can attribute the T_g variation essentially to the length of the polyether chain between two acrylic double bonds. By plotting the T_g values obtained by TMA as a function of the reciprocal value of the chain length, M_c , a linear plot according to the Nielsen equation was obtained (Fig. 6). The intercept T_g value, at zero crosslinking density, is about -88°C , in good

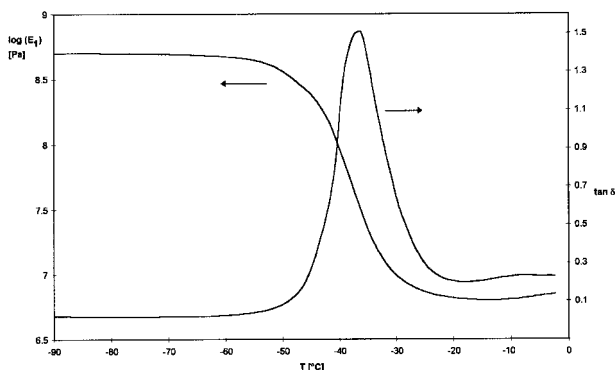


Figure 5 DMTA spectrum of UV-cured PPGDA 1000 film.

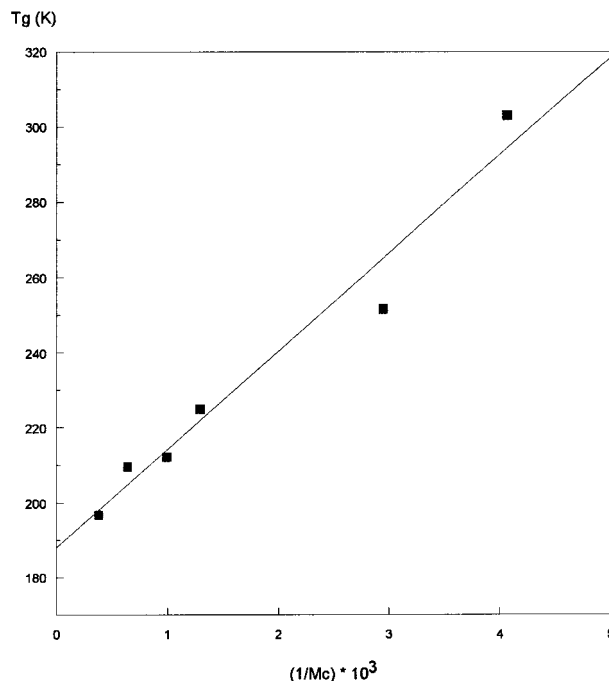


Figure 6 T_g versus $1/M_c$ for UV-cured PPGDA oligomers.

agreement with the T_g of PPG reported in the literature (-72°C).¹²

We can conclude that a good correlation of the network properties as a function of crosslinking density for UV-cured PPGDA oligomers is evident, as observed for PEGDA and PTMEGDA oligomers.^{1,2} In spite of the possible network irregularities (network inhomogeneities, low values of acrylic functionality, cyclization reactions⁹), the investigated systems behave rather like a regular model network.

Table III collects the values of the solubility parameters (δ) of PPG, PTMEG, and PEG calculated taking into account the dispersion, polar, and hydrogen bonding contributions.¹³ The obtained values indicate a decrease of δ in the order: PEGDA > PPGDA > PTMEGDA. The same behavior is observed by comparing the equilibrium swelling values in water at 25°C of UV-cured acrylated oligomers having the same MW. PPGDA oligomers show intermediate values between PEGDA and PTMEGDA products. Moreover, the swelling ratios in water of the cured films increase by increasing the oligomer MW, that is, by decreasing the network crosslinking density.¹⁴ The data are reported in Table IV.

Table III Solubility Parameters for PEG, PPG, and PTMEG Oligomers

Oligomer	$\delta_d = \frac{\sum F_{di}}{V}$	$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V}$	$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}}$	$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$ (MPa ^{1/2})
PEG	17.30	10.81	9.00	22.30
PPG	17.00	7.80	7.70	20.20
PTMEG	16.80	5.70	6.50	18.90

Properties of Epoxy-Acrylate Resin/PPGDA Mixtures

With the aim of evaluating the flexibilizing effect of PPGDA oligomers on a rigid network, 40/60 w/w mixtures with BGEDA resin were prepared and subjected to UV curing. In Table V, some properties of the UV-cured films are reported. First, the double bond conversion was found to increase in the presence of the PPGDA oligomers. The pure epoxy-acrylate resin shows only about 65% double bond conversion,¹⁵ whereas in the presence of PPGDA oligomers, the conversion clearly increases. Moreover, the double bond conversion increases by increasing the MW of the PPGDA oligomers, indicating that a higher flexibilizing effect is obtained in the presence of the higher MW oligomers.

The T_g values obtained by means of DSC and TMA analyses are reported in Table V. Pure epoxy-acrylic resin shows a very high T_g value

Table IV Equilibrium Swelling in Water (%) at 25°C for UV-Cured PEGDA,^a PPGDA, and PTMEGDA^b Oligomers

Oligomer	Swelling (%)	Oligomer	Swelling (%)
TEGDA	16.4	PPGDA 2000	13.3
PEGDA 400	34.1	PPGDA 4000	15.5
PEGDA 600	40.2	TMGEDA	0
PEGDA 1000	82.0	PTMEGDA 250	1.7
TPGDA	0.2	PTMEGDA 650	5.6
PPGDA 400	4.1	PTMEGDA 1000	6.9
PPGDA 725	6.6	PTMEGDA 2000	9.6
PPGDA 1000	8.8		

^a Ref. 1.^b Ref. 2.

(>100°C)¹⁵; in the presence of PPGDA, a strong decrease of the T_g is observed, due to the flexibilizing effect of the oligomers. Moreover, the T_g values decrease by increasing the MW of PPGDA. In Table V, a sample containing PEGDA 600 is included for comparison. It can be noted that the flexibilizing effect of PPGDA is, under the same conditions, clearly higher with respect to PEGDA, in agreement with its lower T_g value.

Finally, Table V collects equilibrium swelling values in water at 25°C of the cured films. By increasing the MW, the swelling increases due to the decreasing of the network crosslinking density, as observed considering the pure PPGDA oligomers.

CONCLUSIONS

The following main conclusions can be drawn. During the preparation of PPGDA oligomers, a decrease of MW was found, the acrylic functionality remaining constant. This trend was attributed to a hydrolytic attack on the PPG chain. The double bond conversion is always complete, with the exception of the TPGDA oligomer. The T_g values of the cured films increase by decreasing the oligomer MW, that is, by increasing the network crosslinking density, and a linear plot of T_g values versus the reciprocal of the value of the chain length was obtained, according to the Nielsen equation. The swelling ratios in water of the cured films increase by increasing the oligomer MW. At constant MW, swelling of PPGDA is intermediate between PEGDA and PTMEGDA, according to the solubility parameter values. By considering mixtures with a typical epoxy-acrylate resin, a high

Table V Properties of UV-Cured Epoxy-Acrylic Resin-PPGDA 60/40 w/w Mixtures

Oligomer	d.b. conv. (%) ^a	Swelling (%) ^b	T_g (DSC) (°C)	T_g (TMA) (°C)	Gel Content (%) ^c
BGEDA	65.0	0	>100		97.1
TPGDA	85.7	1.26	30.7	22.8	99.9
PPGDA 400	80.6	1.95	18.3	10.4	95.5
PPGDA 725	89.7	3.96	-14.7	-21.1	97.8
PPGDA 1000	89.9	5.13	-20.9	-26.8	96.3
PPGDA 2000	93.8	6.30	-31.6	-32.5	96.2
PPGDA 4000	90.9	6.64	-36.7	-40.2	94.4
PEGDA 600 ^d	89.5	9.60		19.1	99.2

^a By FTIR analysis.^b In water at 25°C.^c By CHCl₃ treatment.^d $\bar{M}_n = 733$.

flexibilizing effect of PPGDA oligomers was observed.

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