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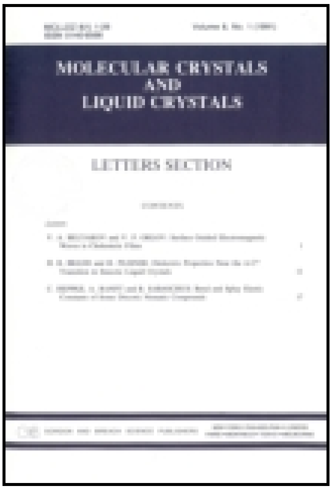

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Jae Hwan Chun[a][b], Jung Mi Cheon[a], Boo Young Jeong[a] & Nam Ju Jo[b]
[a] Polymer Surface Research Team, Korea Institute of Footwear and Leather Technology, Pusan, Korea
[b] Department of Polymer Science Engineering, Pusan National University, Pusan, Korea
Published online: 17 Nov 2014.

To cite this article: Jae Hwan Chun, Jung Mi Cheon, Boo Young Jeong & Nam Ju Jo (2014) Synthesis of Poly(methylene oxy-alt PPO)glycols and Its Effect on the Properties of Polyurethane UV-Cured Film, Molecular Crystals and Liquid Crystals, 600:1, 63-69, DOI: 10.1080/15421406.2014.936775

To link to this article: http://dx.doi.org/10.1080/15421406.2014.936775

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Mol. Cryst. Liq. Cryst., Vol. 600: pp. 63–69, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.936775

Synthesis of Poly(methylene oxy-alt PPO)glycols and Its Effect on the Properties of Polyurethane UV-Cured Film

JAE HWAN CHUN,[1,2] JUNG MI CHEON,[1]
BOO YOUNG JEONG,[1] AND NAM JU JO[2,*]

[1]Polymer Surface Research Team, Korea Institute of Footwear and Leather Technology, Pusan, Korea
[2]Department of Polymer Science Engineering, Pusan National University, Pusan, Korea

In this study, we synthesized MPPG including the methylene-oxy group from polypropylene glycol (PPG) with the molecular weight (g/mol) of 200. Also UV curable resins were prepared from the mixture of polyurethane acrylate (PUA) oligomer which was synthesized with synthesized MPPG, TMPTA, HDDA, and HP-8 to investigate the possibility of its application for optical film materials. The T_g *was higher for UAMP oligomer with MPPG as well as MPPG than that of PPG and UAP oligomer. The refractive index and the pencil hardness of UCM were higher than those of UC while the optical transmittances of UCM and UC were much the same.*

Keywords Poly(methylene oxy-alt PPO)glycols; UV curing; surface hardness

Introduction

With the popularization of smart phones, the demand for high-performance coating materials in the field of displays, optical components, and precision electronic components has increased. Polyethyleneterephthalate (PET) film is widely used in a various optical elements such as mobile phone, display pannel, notebook, etc. As a protective layer, PET films exhibit important optical elements specifically the surface treatment layer. The resin composition of this surface treatment layer needs high hardness and excellent optical properties such as transparency and excellent resistance to yellowing. A resin composition having excellent optical properties can be obtained by using the active energy ray-curable acrylic resin [1, 2]. A UV curable system has received increasing attention on account of its fast curing and low energy consumption. The UV curable system is typically composed of reactive oligomers, reactive diluents, and photoinitiators [3]. Reactive urethane oligomer is the most important component in determining the ultimate physical properties of UV-cured coatings. Typically it is segmented polyurethane oligomer tipped with acrylic functionality

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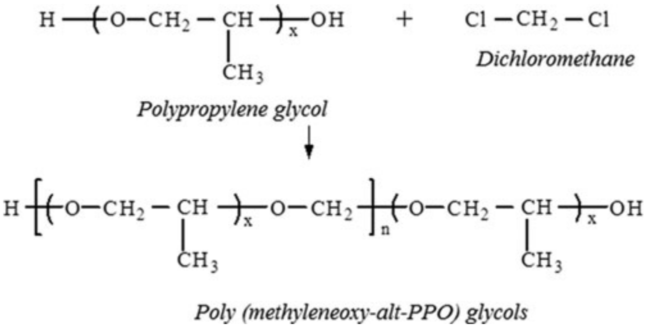
[*] Address correspondence to Prof. Nam-Ju Jo, Dept. of Polymer Science Engineering, Pusan National University, Busan 609-735, Korea. Tel.: (+82)51-510-2462; Fax: (+82)51-513-7720. E-mail: namjujo@pusan.ac.kr

such as 2-hydroxy ethylacrylate and 2-hydroxyethyl methacrylate. The microphase separation of the urethane segments, which is mainly governed by the soft segment length and type, is a key parameter to control the dynamic mechanical properties of the PU acrylates [4]. In general, polyurethane acrylates have the potential to combine the high abrasion resistance, toughness, tear strength, and good low temperature properties of polyurethane with the superior optical properties and weatherability of polyacrylates [5]. Polyether polyols are used as soft segments for UV curable oligomers, as a consequence of their excellent hydrolytic stability and availability in non-solvent oligomer preparation due to their low viscosity. However, as the cohesive force of these polyols is low, we modified polypropylene glycol to form non-covalent interaction such as hydrogen bond by increasing oxygen density. In this study, we synthesized poly(methylene oxy-alt PPO)glycols (MPPG) including the methylene-oxy group from polypropylene glycol with the molecular weight (g/mol) of 200 and we studied the effects of PU soft segment modification on the properties of PU acrylates (PUA). In addition, we considered the preparation and properties of UV curable resin to investigate the possibility of its application on optical film materials.

Experiment

Polypropylene glycol (PPG, Mn = 200, 1000, 2000 g/mol, KPX Chemical) was dried at 80°C under 0.1 mmHg until no bubble was observed. Dichloromethane (DCM, Aldrich Chemical), tetrabutylammonium bromide (TBAB, Aldrich Chemical), sodium hydroxide (NaOH, Aldrich Chemical) tetrahydrofuran (THF, Aldrich Chemical), isophorone diisocyanate (IPDI, Aldrich Chemical), 2-hydroxyethylmethacrylate (2-HEMA, Aldrich Chemical), trimethylolpropane triacrylate (TMPTA, Miwon Specialty Chemical), hexanediol diacrylate (HDDA, Miwon Specialty Chemical), and Micure HP-8 (Miwon Specialty Chemical) were used without further purification and the modification of PPG was carried out. 33.3 g of PPG (M_n = 200 g/mol) dissolved in THF and 16 g of NaOH was added in the mixture where approximately 2.7 g of TBAB and 28.3 g of DCM at 40°C were added before the reaction was allowed to proceed for 8 hours (Scheme 1). Polyurethane acrylate oligomers (UAP and UAMP) were synthesized by the reaction of PPG or synthesized MPPG and IPDI using DBTDL as the catalyst. The reaction was performed at 70–80°C under a dry nitrogen atmosphere for 5 h. The polyurethane prepolymer obtained was cooled to 50°C and then 2-HEMA was added into the mixture. The reaction was monitored for about 2 h until the signal for the –NCO group (at 2270 cm^{-1}) in the IR spectrum disappeared. UV curable resin was obtained by adding TMPTA and HDDA and HP-8 to prearranged PUA oligomers (Table 2). UV cured film was prepared by coating on a PET film using a 25 μm applicator and irradiation using a medium pressure mercury lamp (lamp power: 100 W/cm, UV energy density: 1072 mJ/cm^2, fusion system).

The chemical components of MPPG and PUA oligomers were confirmed by the Fourier transform infrared spectrometer (FT-IR, Jasco 430). For each IR spectrometer sample, 32 scans at a 4-cm^{-1} resolution were collected in the transmittance mode. The ^{1}H-NMR spectra of MPPG was recorded in a 500 MHz Fourier transform-nuclear magnetic resonance spectrometer (FT-NMR, Unity-Inova 500). The molecular weights of MPPG and PUA oligomers were obtained using a gel permeation chromatography (GPC, waters: Pump 590, RI 410, Integrator 745B). The thermal property of the samples was measured using differential scanning calorimetry (DSC, TA instrument Q-100) during the second heating (10°C/min). The refractive index and optical transmittance of the UV curable resins were measured using prism coupler (2010/M, Metricon) and spectrophotometer (V-670, Jasco)



Scheme 1. Synthesis process for the poly(methylene oxy-alt PPO)glycols.

respectively. The UV-cured film properties were characterized using ASTM standards such as pencil hardness (ASTM D-3363).

Results and Discussion

We synthesized poly(methyleneoxy-alt-PPO)glycols including methylene-oxy group from PPG with the molecular weight (g/mol) of 200. The molecular weight of the modified polyol that was obtained by GPC was confirmed in Table 1, with the molecular weight and polydispersity index of the modified polyol being 1602 g/mol and 1.12, respectively.

FT-IR was measured in order to identify the structure of MPPG. Figure 1 shows the FT-IR spectra of PPG and MPPG. The spectra of polyol show absorption bands at 3200–3550 cm^{-1}, which is the terminal -OH stretch of polyol. The PPG and MPPG present the characteristic peaks of the $-CH_3$ stretch band at 2970 cm^{-1} and the -C-O-C- stretch band of the aliphatic ether at 1110 cm^{-1}, 1020–1030 cm^{-1}. The band of the aliphatic ether of MPPG is observed at about 1030 cm^{-1} to the left of the band (1020 cm^{-1}) of PPG. These results confirm that this band of the MPPG appears at higher frequencies and is a much stronger absorption than PPG by incorporating methylene-oxy- group into the PPG. Its chemical structure can be specified using ^{1}H-NMR spectroscopy also. The result of the chemical shift of the MPPG is shown in Figure 2 and the proton corresponding to each resonance peak was marked in that. The repeating unit of the polypropylene oxide (PPO) has characteristic chemical shifts in spectrum depending on the proton attached to MPPG. The signal at 1.1 ppm, 1.7 ppm, and 3.2–3.9 ppm can be attributed to protons of the CH_3

Table 1. Composition of the PU-acrylate oligomers

	Equivalent ratio			
Sample code	Polyol		IPDI	2-HEMA
UAP1000	PPG1000	1	1.25	0.25
UAP2000	PPG2000	1	1.25	0.25
UAMP	MPPG[a]	1	1.25	0.25

[a] Mn: 1602(g/mol), Mw: 1796(g/mol), PDI: 1.12

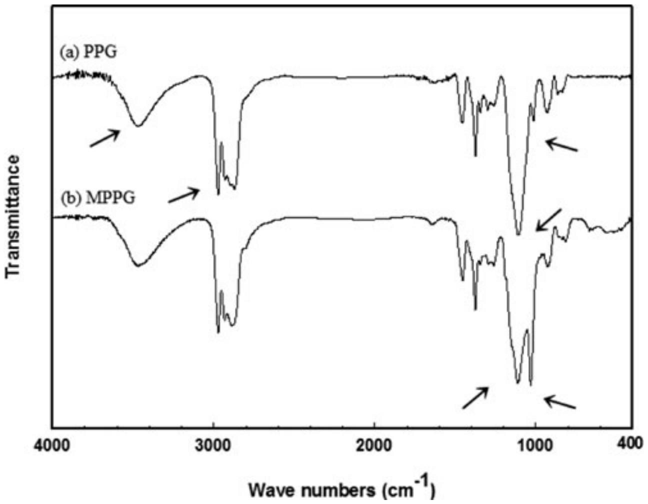


Figure 1. FT-IR spectra of polyol: (a) PPG200 and (b) MPPG).

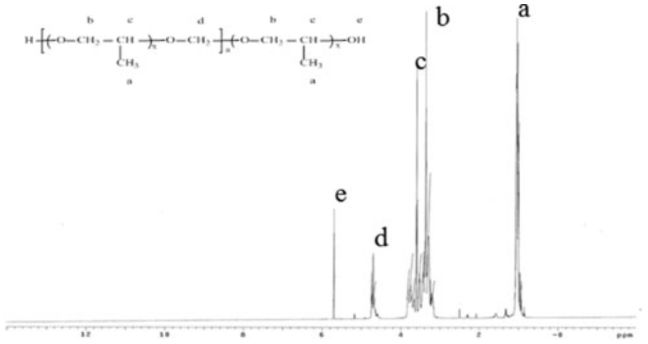


Figure 2. ^{1}H FT-NMR spectrum of the poly(methyleneoxy-alt-PPO)glycol (MPPG).

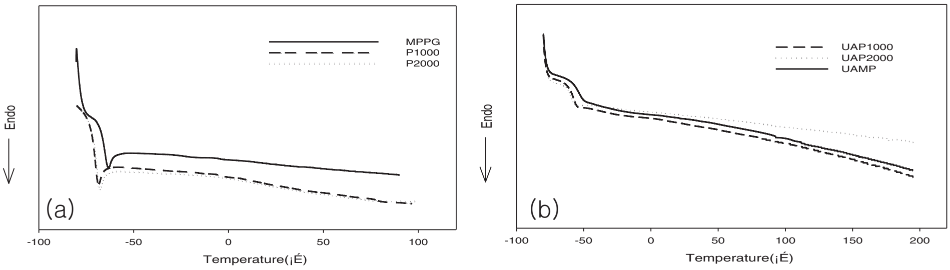


Figure 3. DSC thermograms of polyols(a) and PUA oligomers(b).

Table 2. Composition of the UV-curing resin

	Oligomer (wt%)			Monomer (wt%)					
Sample code	UAP1000	UAP2000	UAMP1500	TMPTA	HDDA	Photo initiator (wt%)	Refractive index	Optical transmittance (%)	Pencil hardness
UC1000	55			40		5	1.489	95% >	HB
UC2000		55		40		5	1.488	95% >	HB
UCM1			55	40		5	1.498	95% >	H
UCM2			75	20		5	1.493	95% >	HB
UCM3			85	10		5	1.493	95% >	HB
UCM4			55	32	8	5	1.494	95% >	HB
UCM5			55	24	16	5	1.496	95% >	HB

group, CH_2 group, and CH group, respectively, in PPO. The attached protons of the CH_2 group of methylene-oxy group also contribute to the signal at 4.7 ppm. The resonance peak of the protons of the terminal hydroxyl group occurred at 5.7 ppm. Based on this result, it was found that the MPPG was well-synthesized.

Figure 3 shows the 2nd heating curve of the DSC of polyols and PUAs. As presented in Figure 3, the T_g of modified polyol from PPG 200 (Mn = 200 g/mol), whose average molecular weight (Mn) is 1602 g/mol, is measured at −65.1°C. This increases more than T_g from the original PPG1000 and PPG2000, −70.8°C and −71.2°C respectively. This tendency becomes more pronounced as preparation of PUA. The T_g of prepared PUAs using the PPG 1000, PPG 2000, and MPPG is measured at −57.6°C, −58.8°C, and −52.38°C, respectively. The T_g of the soft segment shifts to a higher temperature by using MPPG. In conclusion, the T_g of the polyol is changed compared with original polyols because increasing oxygen density hinders the rotational motion through the methylene-oxy unit attached to the main chain of the PPG. The result of PUA also indicates that when methylene-oxy ($-CH_2O-$) group is attached in the main chain of PPG, non-covalent interaction, such as the hydrogen bond between the urethane groups and polyols, occurs more compared to unmodified polyols [6].

The refractive index results in Table 2 show that the refractive index of UCM series is higher compared with UC. In the formulation of UCM series, the refractive index decreases slightly with increasing UAMP oligomer content. Generally, since the refractive index of matter is dependent on the density of the matter, these results may be related to a dense structure. An MPPG-based system shows a higher index than the original polyol-based system. The reason for this is the MPPG-based system is a denser structure than the PPG based system. The UV–Vis spectra of UV curable resin are found in Table 2. As can be observed, all the results of UC and UCM series display high transparency (more than 95%) throughout the visible light range of 400-800 nm regardless of PUA oligomer types. Transmittance of optical resin is an important factor engaged with pencil hardness in an optical protective film. This shows that the internal structure of PUA oligomer with MPPG rarely truns the optical transmittance down. A summary of the pencil hardness is found in Table 2. UV-cured film using the PUA oligomer of MPPG type shows a higher pencil hardness than that of PPG type when the oligomer content of 55% and TMPTA as reactive diluent were used. The result of surface hardness from PUA oligomer using MPPG can be attributed to the increase in non-covalent interaction. The hydrogen bonds play a dominant role on hardness and favor its improvement.

Conclusion

In this paper, we have successfully synthesized the modified polyol under phase transfer catalysis reaction which was used in PUA oligomers as soft segment. The chemical structure of MPPG was investigated by FT-IR and ^{1}H-NMR measurements. The T_g was higher for PUA oligomer with MPPG as well as MPPG than for original PPG and PUA oligomer with original PPG. We prepared UV curable resin using synthesized PUA oligomer, which was applied on protective film for optical element use. It was found that the value of the refractive index and the pencil hardness of UCM were higher than those of UC, and the optical transmittances of UCM and UC were much the same. These results show that the hydrogen bond between the urethane groups and polyols occurs more compared to unmodified polyols by introducing the methylene-oxy ($-CH_2O-$) group in the main chain of PPG. The hydrogen bonds play a dominant role in hardness and favor its improvement. Pencil hardness transmittance of optical resin is an important factor as an optical protective film. The results show a possibility to apply the findings to protective films in optical elements.

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