Research Article

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Synthesis and properties of polyurethane acrylate oligomer based on polycaprolactone diol

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Abstract: The polycaprolactone diol (PCL diol) was prepared by ring-opening polymerization method, with hydroquinone bis(2-hydroxyethyl) ether as the reactive initiator and ϵ -caprolactone as the monomer. The polyurethane acrylate (PUA) was prepared with the self-made PCL diol. Then, PUA was used to prepare the ultraviolet curable coatings. The structure and molecular weight of PCL diol was characterized by Fourier transform infrared spectroscopy, gel-permeation chromatography, and hydroxyl value titration. The performance of the cured coating film was characterized by thermogravimetric analysis and scanning electron microscope. The flexibility and hardness of the cured coating film were tested. The results showed that the narrow molecular weight PCL diol was successfully synthesized. The UV curing coating film had the optimal performance with a hardness of 3H, flexibility of 1.5 mm, abrasion resistance of 0.028 g^{-1} , and adhesion of grade 1, all coating films showed good thermal properties.

Keywords: hydroquinone bis(2-hydroxyethyl) ether, polycaprolactone diol, UV curing coating

1 Introduction

Polycaprolactone diol (PCL diol) (1) is formed by ring-opening polymerization of ϵ -caprolactone (ϵ -CL) monomer under the action of initiator and catalyst (2–4). ϵ -CL monomer can undergo addition reactions with many functional groups, such as hydroxyl ($-\text{OH}$) and amino ($-\text{NH}_2$), without destroying the structure of the functional group or generating by-products. The synthesized PCL diol is

widely used in the fields of polyurethane elastomers, coatings, and adhesives (5–9).

This article uses hydroquinone bis(2-hydroxyethyl) ether (HQEE) (10,11) as the initiator for the synthesis of PCL diol. As a small molecule diol, it has a rigid symmetrical structure, with a high melting point (120°C) and crystallinity. The synthesized PCL diol with HQEE has the flexibility of ϵ -CL and the hardness and abrasion resistance of HQEE.

With the increasing attention to environmental issues on a global scale, coatings are facing huge challenges. Ultraviolet (UV) curing technology has the characteristics of fast curing at room temperature, no volatile organic compounds, high efficiency, and adaptability to many substrates. It can be widely used in high-tech industrial fields such as metal coatings, protective coatings, and electronic packaging coatings (12–15).

Polyurethane acrylate (PUA), as a commonly used oligomer in UV curing coatings (16–21), has the advantages of high adhesion, good wear resistance, and anti-aging resistance, as well as good weather resistance and optical properties. In order to improve the comprehensive performance of the cured coating which is applied on the ployvinyl chloride (PVC) floor, a novel PUA was synthesized with HQEE as the initiator, and the photocuring behavior of the coating film was discussed.

2 Experiment

2.1 Materials

ϵ -CL was purchased from Hunan Juren Chemical New Materials Technology Co., Ltd. Vacuum distillation treatment was performed for half an hour before use. HQEE and organic bismuth were purchased from Aladdin Reagent Co., Ltd. Isophorone diisocyanate (IPDI), hydroxyethyl acrylate (HEA), dibutyltin dilaurate (DBTDL), epoxy acrylic resin (EA), 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173), methyl benzoylformate (MBF), tripropylene glycol diacrylate (TPGDA),

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trimethylolpropane triacrylate (TMPTA), polycarbonate diol (PCDL), and PUA (6303) were from Kayin Chemicals. Polyethylene glycol (C2020) was from Wanhua Chemical Group Co., Ltd. Di-*n*-butylamine, toluene, bromocresol green, acetone, isopropanol, hydrochloric acid and ethyl acetate, all of which were of analytical grade, were from Guangzhou Chemical Reagent Factory.

2.2 Preparation of PCL diol

The polymerization was carried out by ring-opening polymerization method under nitrogen atmosphere in 500 mL four-neck flask equipped with a stirrer, a condensation tube, and a centigrade thermometer. ϵ -CL monomer, HQEE, and catalyst were added to the four-neck flask according to the measured molar ratio. The reaction temperature and reaction time were set for a specific period. After the reaction is finished, the product was stored in a desiccator for later use (Figure 1).

2.3 Preparation of PUA

Step 1: The polymerization was carried out under nitrogen atmosphere in 500 mL four-neck flask equipped with a stirrer, a condensation tube, and a centigrade thermometer. 0.4 mol IPDI and 0.045 g DBTDL (0.05% of the mass fraction of IPDI) were added to the four-neck flask and the temperature was increased to 55°C. Then, 0.4 mol HEA was added dropwise for about 1.5 h, keeping the reaction temperature at 55°C, and the –NCO value was titrated every half an hour after the dropping, until the –NCO reaches the theoretical value.

Step 2: 0.2 mol PCL diol and DBTDL (0.05% of the mass fraction of PCL diol) were added to the four-neck flask and the temperature was increased to 65°C. Then, the prepolymer synthesized in step 1 was added dropwise

for about 1.5 h, keeping the reaction temperature at 65°C, and the –NCO value was titrated every half an hour after the dropping until the –NCO content is less than 0.5% and then a little HEA (1% of the mass fraction of PCL diol) was added to eliminate extra –NCO content (Figure 2).

2.4 Preparation of coating film

For preparing the UV curing coating 45 parts PUA, 5 parts EA, 10 parts TMPTA, 36 parts HDDA, 2 parts 1173, and 2 parts MBF were mixed and magnetically stirred for about 0.5 h, and then the mixture was applied on a polished and dried tinplate sheet. The coating film of thickness 20 μm was then irradiated by a UV curing machine, the surface drying time was measured by the finger touch method.

3 Characterization

3.1 Fourier transform infrared (FTIR)

The FTIR spectra of samples were collected by Bruker Equinox 55 spectrophotometer, Germany. The scanning region was 4,000–500 cm^{-1} . The samples were analyzed by applying on KBr disks.

3.2 $^1\text{H-NMR}$

The $^1\text{H-NMR}$ spectrometer is Bruker 400M from Bruker, Germany. CDCl_3 is the solvent and TMS is the internal standard.

3.3 Gel permeation chromatography (GPC)

Molecular weight and distribution index (polydispersity index, PDI) of PCL diol were obtained using a GPC equipped with Shodex RI-201H differential refractive index detector and Shodex KF-805 column system, using tetrahydrofuran as eluant at a flow rate of 1.0 $\text{mL}\cdot\text{min}^{-1}$.

3.4 Scanning electron microscope (SEM)

The UV-curable coating film was coated with the gold-palladium film and examined by a field emission SEM (EVO18, Zeiss, Oberkochen, Germany).

Figure 1: Synthesis of PCL diol.

Figure 2: Synthesis of PUA.

3.5 Thermogravimetric analysis (TGA)

The differential thermal-thermogravimetric synchronization analyzer is Shimadzu DTG-60(H). The sample (5–8 mg) was heated from room temperature to 600°C at a heating rate of 10°C·min⁻¹ under N₂ flow rate of 100 mL·min⁻¹.

3.6 Performance test

Hydroxyl values of PCL diol was measured according to ISO 14900:2001. The viscosities of PCL diol were surveyed at 25°C through Brookfield LVT rotational viscometer. NCO content was determined according to GB/T 18446-2009. UV curing time was determined according to GB/T 1728-1979. The abrasion resistance was determined according to GB/T 1768-2006.

Adhesion was determined according to GB/T 9286-1998. The hardness of the coating film was determined according to GB/T 6739-1996. Flexibility was determined according to GB/T 1731-1993. Storage stability was determined according to the provisions of GB/T 33327-2016. Water resistance, alkali resistance, alcohol resistance, and pollution resistance were determined according to the provisions of GB/T 30648.4-2015.

4 Results and discussion

4.1 Discussion on synthetic conditions of PCL diol

Figure 3 shows the effect of reaction temperature on the number-average molecular weight (M_n) and PDI of PCL

diol. With the increase in the reaction temperature, the M_n and PDI of PCL diol increase. When the reaction temperature is 130°C, the M_n is 540, while the M_n of the PCL diol has not reached the set value. When the reaction temperature is higher than 170°C, the M_n of PCL diol far exceeds the theoretical molecular weight, and the PDI of PCL diol is relatively broad, which may be due to the breaking of the ether bond in HQEE. When the reaction temperature is 150°C, the M_n of PCL diol measured by GPC is 1,386, which is 57% higher than the theoretical design molecular weight of 882. This is due to the hydrodynamic volume of the polyester and the polystyrene standard samples. When measuring low relative molecular M_n , the polystyrene standard curve will cause the measured M_n to be 50–100% higher than the actual value (22). In addition, the PDI at this temperature is 1.28, which is relatively narrow. Therefore, if the temperature

Figure 3: The effect of reaction temperature on the M_n and PDI of PCL diol (the reaction temperature was 150°C).

Figure 4: The effect of reaction time on the M_n and PDI of PCL diol (the reaction time was 5 h).

is too low or too high, it is not conducive to the polymerization of PCL diol. The suitable reaction temperature in this system is 150°C.

Figure 4 shows the effect of reaction time on the M_n and PDI of PCL diol. With the increase in the reaction time, the M_n and PDI of PCL diol increase. When the reaction time is 2 h, the M_n is 583, while the molecular weight of PCL diol has not reached the set value (22). When the reaction time is more than 6 h, the PDI of PCL diol gradually increases, which may be due to the existence of side reactions such as transesterification in the reaction system. Therefore, the appropriate reaction time in this system is 5 h.

4.2 Hydroxyl value and viscosity

We also synthesized PCL diol in three ratios of n HQEE: n ϵ -CL, 1:4, 1:6, and 1:8, respectively, represented by P_1 , P_2 , and P_3 (under the above optimal conditions).

Table 1 shows the hydroxyl ester and viscosity of PCL diol with different molecular weights. The hydroxyl value of the synthesized PCL diol is within ± 5 from the theoretically calculated hydroxyl value. Compared with the commercially available product, it is within a reasonable

Table 1: Hydroxyl ester and viscosity of PCL diol

	Acid value (mg·KOH·g ⁻¹)	Hydroxyl value (mg·KOH·g ⁻¹)	Viscosity (MPa/65°C)
P_1	0.63	175.7	158
P_2	0.55	131.3	242
P_3	0.43	103.7	303

margin of error, and its acid value is also controlled to be below 1, thereby meeting the requirements of commercially available products.

4.3 FTIR

Figure 5 shows the IR spectrum of PCL diol. The IR spectrum shows a strong and broad absorption peak of stretching vibration near 3,456 cm⁻¹, which is due to the strong hydrogen bonding in the related hydroxyl molecules. Sharp absorption peaks appeared at 2,945 and 2,870 cm⁻¹, corresponding to the symmetry of the CH₂ and CH₃ groups related to the antisymmetric stretching vibration. The absorption peak of carbonyl ester group stretching vibration appeared at 1,732 cm⁻¹, the absorption peak of benzene ring appeared at 1,600 cm⁻¹, and the characteristic absorption peak of ϵ -CL group did not appear at 1,650 cm⁻¹, indicating that ϵ -CL completely reacts with the hydroxyl group of the small molecule polyol, which is consistent with the ideal PCL diol spectrum.

Figure 6 shows the IR spectrum of PUA based on PCL diol. The OH stretching vibration absorption peak at 3,500 cm⁻¹ disappears, the stretching vibration absorption peak of the cis-NH bond in -NHCO at 3,345 cm⁻¹ disappears, and the -NCO characteristic peak at 2,240–2,275 cm⁻¹ disappears. The -NCO group has fully reacted. The C=O stretching vibration absorption peak at 1,720 cm⁻¹ indicates the formation of urethane bond. The absorption peak at 1,627 cm⁻¹ is the C=C stretching vibration peak. And the characteristic absorption peak of the C-H bond on the C=C double bond appeared at 816 cm⁻¹, indicating that HEA has been grafted onto the polyurethane, and the PUA was successfully synthesized.

Figure 7 shows the IR spectrum of the coating before and after curing. Comparing the IR spectra before and after curing, the stretching vibration of the acrylic C=C double bond at 1,633 cm⁻¹ and the CH out-of-plane

Figure 5: Infrared spectrum of PCL diol.

Figure 6: Infrared spectrum of PUA.

Figure 7: Infrared spectra before and after curing of the coating.

distortion vibration characteristic peaks on the $\text{CH}=\text{CH}$ double bond near 810 cm^{-1} have disappeared, which proves that the curing of the system is a free radical polymerization with the double bond opened. The $\text{C}=\text{C}$ double bond effectively participates in the photocuring process, and the curing of the coating film has been completed.

4.4 $^1\text{H-NMR}$

Figure 8 shows the $^1\text{H-NMR}$ spectrum of PCL diol. The proton absorption peak of the benzene ring is at the chemical shift of 6.81. The chemical shift of 3.60 is the methylene proton absorption peak connected to the

Figure 8: $^1\text{H-NMR}$ spectrum of PCL diol.

PCL diol terminal hydroxyl group, and the multiple peak at the chemical shift of 4.05 corresponds to the $-\text{CH}_2$ -proton absorption peak connected to the ether bond of PCL. A $\text{C} + \text{C}'$ peak appears at the chemical shift of 2.31, which corresponds to the $-\text{CH}_2-$ characteristic peak connecting PCL to the carbonyl group in the main chain, indicating that PCL diol was successfully synthesized (4,23).

Figure 9 shows the ^1H -NMR spectrum of PUA. The chemical shifts of 5.88 and 6.14, respectively, correspond to the absorption peaks of the two protons on the $-\text{C}=\text{CH}_2$ bond in the urethane acrylate end-capping agent HEA, and an absorption peak appears at the chemical shift of 4.02, corresponding to the main chain. The chemical shift of 6.3 corresponds to the proton absorption peak on the $-\text{NH}-$ bond, indicating that the PUA was successfully synthesized (4).

4.5 Effect of different types of PUA on the coating film

Oligomers are the most important part of UV curable coatings. We have synthesized a series of PUA oligomers with different diols (except for PCL diol, the relative molecular weight of the other diols is 2,000). Among them, the types of diols include PCL diol, polyether binary (C2020), and polyester diol (5,300). Among them, PCL diol have selected molecular weights of 654, 882, and 1,110, respectively, represented by P_1 , P_2 , and P_3 . In addition, we also selected PUA grades for PVC flooring in the market as 6303 for comparison.

Table 2 shows the effect of PUA synthesized by different diols on the properties of UV-cured coating films. From the corresponding results of P_1 , P_2 , and P_3 in the

Figure 9: ^1H -NMR spectrum of PUA.

Table 2: The influence of different PUA types on the properties of UV-cured coating film

	P_1	P_2	P_3	C2020	PCDL	6303
Curing time (s)	10	12	12	10	10	8
Abrasion resistance (g)	0.025	0.028	0.050	0.074	0.059	0.046
Hardness (H)	4H	3H	2H	HB	H	2H
Adhesion (level)	2	1	1	0	1	0
Flexibility (mm)	1.5	1.5	0.5	4	5	5
Water resistance (h)	>24					
Alkali resistance (h)						
Alcohol resistance (h)						
Vinegar resistance (h)	4	6	6	4	2	6

table, it can be seen that when the molecular weight of PCL diol increases, the hardness and wear resistance of the coating film decrease, and the flexibility becomes better. This is due to the increase in the proportion of the introduced CL, which increases the proportion of the soft segment and improves the flexibility of the coating film, while the proportion of the hard segment decreases correspondingly, and its hardness and wear resistance decrease. P_1 , P_2 , and P_3 all reach the PVC floor industry standard HG/T 5369-2018, while P_2 has better cured film performance.

Comparing P_2 with C2020 and 5300, the performance physical properties of the coating film in all aspects is higher than C2020 and 5300. It may be that the structural characteristics of the introduced CL and HQEE cause the performance of P_2 to be better than C2020 and 5300.

Comparing P_2 with the commercially available product 6303, although it is lower in adhesion than the commercially available product, P_2 is superior in terms of abrasion resistance and flexibility.

4.6 TGA

Figure 10 shows the TG curve of the coating film. It can be seen from the Figure 10 that the thermal weight loss range of the coating film is mainly composed of two stages. The first stage is 100–330°C, and the thermal weight loss is about 10%. The main reason for the thermal weight loss at this stage is the scission of urethane bonds, carbon chains, and ureido bonds (24–26). It can be seen from the figure that in the first stage, the thermal weight loss of P_3 is the smallest, and the thermal weight loss of P_1 is the largest. The possible reason is that the higher the

Figure 10: Thermogravimetric analysis of cured film.

molecular weight of PCL diol, the stronger the van der Waals force between molecules and the stronger the heat resistance. The second stage is 330–500°C, and the thermal weight loss is about 85%. The main reason for the weight loss in this stage is the crosslinking of the UV-cured double bond (27). At this stage P_1 , P_2 , and P_3 correspond to the starting temperature of thermal weight loss 313°C, 341°C, and 310°C and the end temperature 531°C, 530°C, and 481°C, respectively. P_3 is the first to be completely degraded, which may be due to the increase in the molecular weight of PCL diol and decrease in the degree of crosslinking. The starting temperature and end temperature of P_2 at this stage are better than those of P_1 and P_3 . Therefore, P_2 has better heat resistance.

4.7 SEM

Figure 11 shows scanning electron micrographs of P_2 . The cured film has a little white wrinkles, which may be due

Figure 11: Scanning electron micrographs of P_2 .

to the effect of oxygen inhibition in the photopolymerization system. When the UV curable resin liquid film coated on the substrate is exposed to oxygen under the condition of oxygen under UV light, due to the quenching of free radicals by oxygen, a thin monomer liquid film remains uncured on the surface (18,28). The uncured liquid layer will spontaneously expand the gradient polymer film constrained by the underlying matrix, causing in-plane stress, and producing surface wrinkle patterns. This can be improved by adding oxygen inhibitors in the later stage. From the figure, we can see that the surface of the cured film is flat and has strong compactness.

5 Conclusion

PCL diol was synthesized by the ring-opening polymerization of ϵ -CL initiated with HQEE. FTIR spectra of PCL diol disclosed that ϵ -CL has reacted with HQEE. GPC and hydroxyl value titration results revealed that the measured M_n approached the theoretical molecular weights with the PDI data range controlled below 1.3. The cured coating film based on PCL diol had a hardness of 3H, a flexibility of 1.5 mm, abrasion resistance of 0.028 g^{-1} , and an adhesion level of 1, and excellent heat resistance and microscopic morphology.

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