

Cationic CO₂-based Waterborne Polyurethane with High Solid Content and Excellent Ageing Resistance

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 Electronic Supplementary Information

Abstract High solid content CO₂-based cationic waterborne polyurethanes (CWPU) were prepared using CO₂-polyols as soft segment and *N*-methyl diethanolamine (MDEA) as hydrophilic group. The resulting stable aqueous dispersion displayed a high solid content of 52% with a low MDEA loading of 3.52 wt%. This novel structural CWPU can provide excellent adhesive strength, whose T-peel strength could reach 173.48 N/5cm, 20% higher than that of ester-based cationic waterborne polyurethane (87.55 N/5cm). The CO₂-based CWPU film showed only 2 wt% swelling percentage after 240 min immersion in water, and no change was observed during its immersion in 5 wt% sodium hydroxide solution. The tensile strength of CO₂-WPU dropped slowly to 91.2% after 480 min immersion in a 5 wt% sodium hydroxide solution, whereas that of ester-based CWPU dropped quickly to 32% after 240 min and their mechanical properties were lost after 360 min immersion. Meanwhile, the retention of the tensile strength of the CO₂-CWPU was 81.5% even after 720 min immersion in 10 wt% H₂O₂ solution, while it was only ca. 38% for the ester-based CWPU. These results indicated that the cationic CO₂-based CWPU may be promising waterborne adhesive with outstanding ageing resistance due to its synergistic effect from carbonate and ether groups of CO₂-polyol structure.

Keywords Cationic waterborne polyurethane; CO₂-polyol; High solid content; Hydrolysis/oxidation resistance

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INTRODUCTION

Polyurethanes (PU) are a class of versatile materials that find application in many fields such as paints, textile, adhesives, foams, etc.^[1–6] Due to worldwide restriction on volatile organic chemicals (VOCs), it is promising to develop waterborne polyurethanes (WPU) to replace conventional organic solvent-based system.^[7–13] WPU is a binary colloidal system in which PU resins are nanodispersed in water medium. However, compared with conventional solvent-based polyurethanes, a very slower drying rate is found in WPU due to the high evaporation heat of water.^[14] Therefore, the long drying time and high energy consumption seriously hindered the development of waterborne system.^[15,16] An important method to solve this problem lies in the increase of the solid content of WPU through the decrease of water content, achieving advantages of reduced film drying time, production and transport costs.^[17,18] Therefore, research nowadays is mainly focused on the preparation of WPU with a high solid content (HSC), which is of growing interest both in the field of scientific research and

industrial applications.^[19,20]

On the other hand, WPU with an HSC inevitably result in a high viscosity which restricts their practical applications. Up to now, there are two ways to solve the contradictory between high solid content and low viscosity: one is the preparation of WPU with multimodal particle size distribution (PSD) and the other was the introduction of ionic and nonionic monomers. For example, He *et al.*^[21] synthesized high solid content (50%) WPU with a low viscosity through enlarging particle size and broadening PSD by virtue of decreasing volume fraction and distance between particles. Peng *et al.*^[22] reported a one-pot method to synthesize HSC WPU by flexible control of bimodal PSD using poly(butylene adipate glycol) (PBA) and propylene oxide glycol (PPG) as the mixed soft segments. Zhang *et al.*^[14] also reported 50% solid content WPU with multimodal PSD using trifunctional siloxane and PPG as the mixed soft segments. Therefore, controlling of particle size and its distribution is crucial to afford WPU with high solid content and low viscosity, as small particles are able to fit into the interstices between large particles.^[23,24] Alternatively, Hou *et al.*^[25] synthesized an anionic WPU with a high solid content of 52% *via* the combination of ionic (dimethylol propionic acid, DMPA) and nonionic (PEG) monomers, whose synergistic effect results in finer particle size and more stable dispersion. The above two approaches open up new avenues for preparing qualified WPU with high

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solid content, whereas, the tedious polymerization steps involved in multimodal PSD and the poor water resistance derived from ionic and nonionic monomers hinder the potential applications. As an important category of WPU, cationic WPUs exhibit very high adhesion to various ionic substrates, especially for anionic substrates such as leather and glass, leading to important application as adhesives and coagulants.^[26–30] Incorporation of strong polar cationic groups such as *N*-methyl diethanolamine (MDEA) into hard segments of linear PUs can considerably improve polarity, giving cationic WPU with boosted adhesion strength on anionic substrate.^[31–33] Moreover, cationic WPUs exhibit unique characteristics, including stability in acidic conditions, antibacterial properties and dust resistance through electrostatic repulsion, thus, making them high value-added materials.^[34–36] Therefore, it is worthwhile to prepare high solid content and multifunctional cationic WPUs. Li *et al.*^[33] synthesized cationic WPU with a 52% solid content *via* the combination of cationic group MDEA and nonionic segments PEG-based polyoxyethylene alkyl amine, displaying good dispersion stability, small particle size and low viscosity. However, the resulting materials still suffered from poor water resistance owing to the introduction of the nonionic units.

Herein, we reported the development of high solid content cationic WPU with excellent water resistance using CO₂-polyols as soft segments and MDEA as ionic monomer. The key structural feature of CO₂-polyols lies in the coexistence of hydrolysis-resistant ether unit and oxidation-resistant carbonate unit, which endowed targeted properties for the resulting CO₂-based cationic WPU (CO₂-CWPU).^[37] Results showed that an HSC of 52% was obtained for CO₂-CWPU with a low MDEA loading of 3.53% which assured strong adhesive capacity with T-peel strength of 173.48 N/5cm, about 20% higher than that of polyester-based cationic WPU (87.55 N/5cm). Moreover, the CO₂-CWPU displayed excellent mechanical, water-resistance and hydrolysis/oxidation resistance properties, which is a promising waterborne adhesive. The present study provides a platform for designing high-performance cationic WPU using CO₂ as raw materials.

EXPERIMENTAL

Chemicals

The zinc-cobalt double metal complex (Zn-Co-DMC) catalyst was prepared according to the previous reported method.^[38] Propylene oxide (PO) was refluxed over calcium hydride and then distilled under argon atmosphere. Carbon dioxide (>99.99%), *p*-phthalic acid (PTA) (AR, Aladdin), hydrochloric acid (HCl) (AR, Sinopharm), isophoronediiisocyanate (IPDI) (98%, Aladdin), di-*n*-butyl tindilaurate (DBTDL) (95%, Aladdin), 2,2-dimethylol propionic acid (DMPA) (AR, Aladdin), *N*-methyl diethanolamine (MDEA) (AR, Aladdin), 1,4-butanediol (BDO) (AR, Sinopharm), triethylamine (TEA) (AR, Sinopharm), hydrogen peroxide aqueous solution (30%, Sinopharm), sodium hydroxide (97%, Aladdin), and butanone (AR, Sinopharm) were used as received. Poly(butylene adipate glycol) ($M_n=2000$) (PBA-2000) (AR, Sinopharm), and CO₂-polyol were dehydrated under vacuum at 95 °C for 3 h before use.

Characterization

FTIR and ¹H-NMR measurement

FTIR analysis was carried out on a Bruker TENSOR-27

spectrometer at a resolution of 4 cm⁻¹ over a wave number range of 4000–400 cm⁻¹, where the acetone solution of the specimen was cast onto a disk of KBr pellet. ¹H-NMR spectra was recorded by Bruker-300 spectrometer using CDCl₃ as solvent.

DLS measurement

The average particle size and particle size distribution (PSD) of the cationic WPUs were measured using an ALV CGS-3 light scattering spectrometer equipped with an ALV-5000 multitaue digital time correlator and a He-Ne laser ($\lambda=632$ nm). The WPU dispersion was first diluted in deionized water to a concentration of 0.3 wt%, followed by ultrasonic wave treatment to homogenize the dispersion.

DSC measurement

Thermal analysis of the composites was performed under N₂ atmosphere using a TA Instruments differential scanning calorimeter DSC Q20 which was calibrated with a standard indium before measurement. All operations were performed under N₂ atmosphere, and the mass of the sample weights of 5 mg were used. DSC curves were obtained in the temperature range from –50 °C to +80 °C with heating and cooling rates of 5 °C·min⁻¹.

TEM measurement

Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2010 TEM at an acceleration voltage of 200 kV. And the samples were stained by 0.2 wt% phosphotungstic acid hydrate before observation.

The solid content measurement

The solid content of the dispersion was detected by drying it at 80 °C for 48 h and calculating the weight ratio of residue to the dispersion.

Emulsion stability measurement

Every day, 50 mL of latex was placed in a glass bottle at room temperature to observe the condition of the latex, and it was recorded the number of days when sedimentation had occurred.

Preparation of cationic WPU film

The free-standing films of WPUs were prepared according to the following method: the WPUs dispersion were poured into the Teflon disk to dry at room temperature for 7 days and then dried for 24 h in vacuum oven at 40 °C and then stored in a desiccator to avoid moisture.

Stress-strain measurement

For the stress-strain test, the free-standing films were cut into dumb-bell shaped samples with 20 mm length, 0.8 mm thickness and 4 mm width. The tensile stress-strain test was performed on an Instron-1121 at an extension rate of 100 mm·min⁻¹ at 25 °C according to GB 13022-91 and the results quoted were the mean values of three measurements.

Adhesive strength measurement

Adhesive strength was obtained from T-peel tests of solvent-wiped plasticized acrylonitrile butadiene styrene (ABS)/PUDs/solvent wiped plasticized poly(vinyl chloride) (PVC) joints. T-peel strength tests were performed. Before applying the adhesive, the ABS surface was wiped with a dust-free cloth soaked in methyl ethyl ketone allowing the solvent to evaporate for 30 min under open air. Then, the polyurethane dispersions (PUDs) were brushed on ABS with 25 mm × 150 mm × 5 mm in size by a brush, in which a uniform dry solid polyurethane film about 0.25

g weight was formed after 1.5 h water evaporation. And then the heat activated at 65 °C for 5 min, and then the formed adhesive film was heated rapidly to 80 °C under infrared radiation and kept for 10 s. The adhesive joints of PVC strips and ABS were immediately bonded by pressing them together with a pressure of 0.8 MPa for 10 s at room temperature to avoid mismatch and bubble. The T-peel strength was measured in Instron-1121 universal testing machine according to GB/T 2791-1995 after 72 h joint formation using a peel speed of 100 mm·min⁻¹ at 25 °C. The values obtained were the average of three replicates.

Water absorption measurement

The above tensile bars were also used to calculate the water absorption (*A*, %) and swelling ratio (swelling%) of the films, in which *A* (%) can be calculated according to Eq. (1):

$$A(\%) = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where *W*₀ is the weight of the dry sample, and *W*₁ is the weight of the wet films immediately measured after the residual water was removed from the films with a filter paper, in which swelling (%) can be calculated according to Eq. (2):

$$\text{Swelling}(\%) = \frac{L_1 - L_0}{L_0} \quad (2)$$

where *L*₀ is the length of the dry sample, and *L*₁ is the length of the swollen sample.

Synthesis of CO₂-CWPU

CO₂-polyol with 60% carbonate unit content and 1980 g·mol⁻¹ molecular weight was prepared according to previous report by the immortal copolymerization of CO₂ and propylene oxide (PO) using Zn-Co-DMC as catalyst and p-phthalic acid (PTA) as chain transfer agent.^[39] The CO₂-CWPU was synthesized according to a modified acetone process,^[40] where butanone was used as solvent to reduce the viscosity of the reactants and assure the complete chemical reaction (Fig. 1). IPDI and CO₂-polyols were charged in the reactor, catalyzed by dibutyltin dilaurate (DBTDL) in the presence of N₂ atmosphere. The reaction was reacted at 80 °C until the theoretical NCO content of the pre-polymers was reached, as determined by the di-*n*-butylamine titration method. Then, MDEA was added to react for 1 h to afford the backbone with hydrophilicity at 35 °C. After that, BDO was

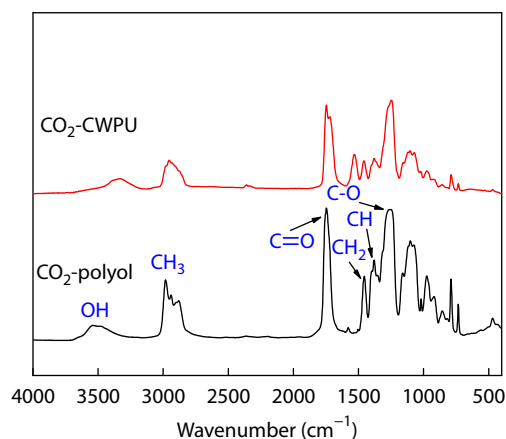


Fig. 1 FTIR spectra of CO₂-CWPU and CO₂-polyol.

added to react for 2 h at 75 °C. The mixture was cooled to 30 °C and butanone (20 wt%) was added at the same time to reduce the viscosity. The neutralization reaction using hydrochloric acid solution proceeded at the same temperature for 30 min. Then, distilled water was added to the reactor and the stirring rate was kept at 600 r/min for 30 min and 300 r/min for another 30 min. Finally, the butanone was removed by rotary evaporator at 50 °C water bath under vacuum to collect the CO₂-CWPU. For reference, PBA-CWPU was prepared in the same procedure, except for the substitution of CO₂-polyol by PBA-2000. The performances of the WPU are listed in Table 1 and the reaction process was illustrated in Scheme 1.

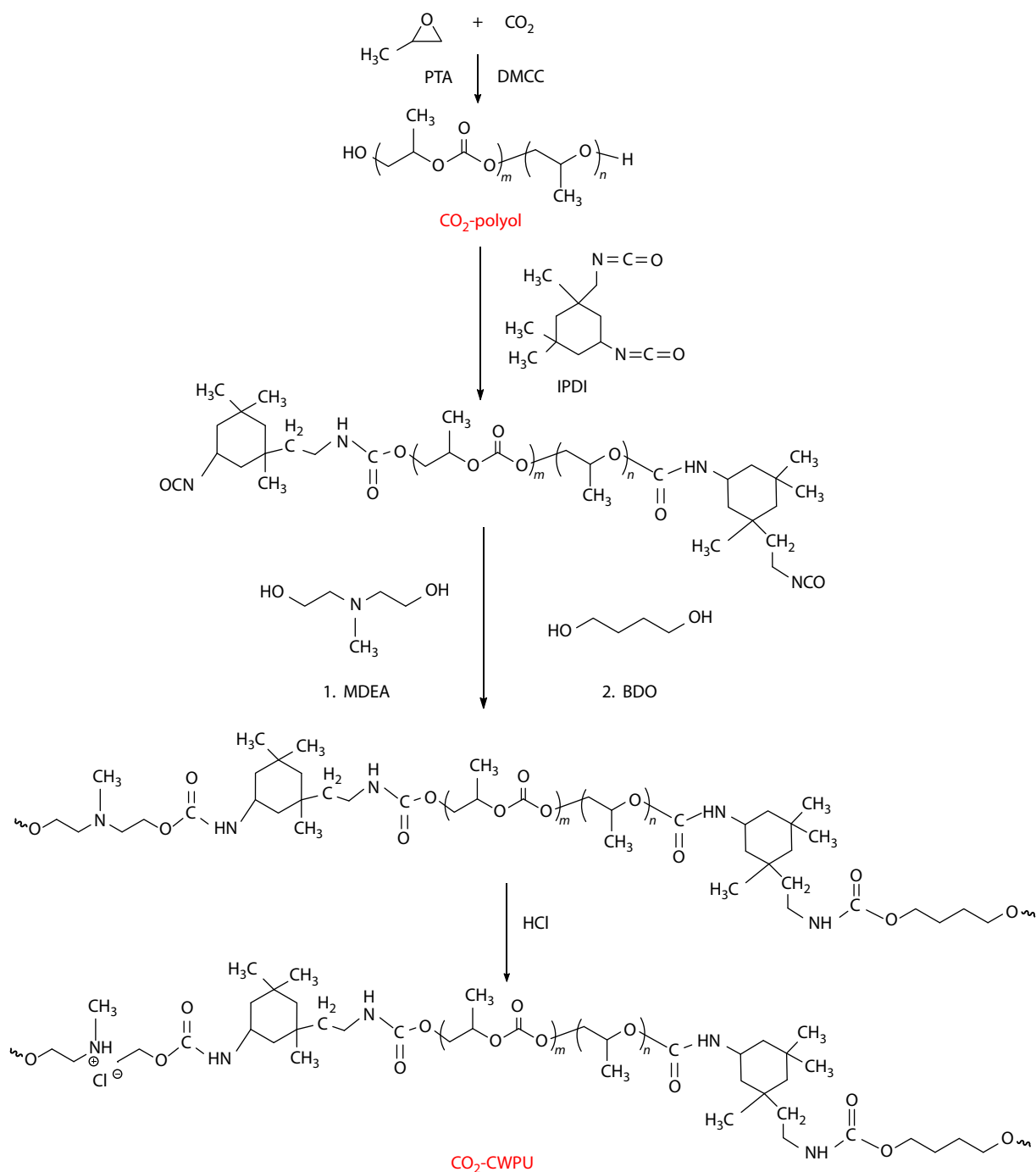
RESULTS AND DISCUSSION

Preparation and characterization of CO₂-CWPU

The synthetic routes to CO₂-CWPU are shown in Scheme 1, in which the OH groups in CO₂-polyol reacted with the NCO units in IPDI, and then hydrophilic monomer MDEA and chain extender BDO were added in sequence. Hydrochloric acid solution was utilized to neutralize the tertiary amine, followed by dispersion with distilled water under high speed. After removal of butanone under vacuum, CO₂-CWPU was obtained. To investigate the effect of MDEA amount on the properties of

Table 1 Composition and performance of CO₂-CWPU.

Samples	PPC-OH (mmol)	IPDI (mmol)	MDEA (mmol)	BDO (mmol)	HCl (mmol)	MDEA (%)	Solid content (%)	Viscosity (cps @ 25°C)	Stability /6 months	T-peel strength (N/5cm)
CO ₂ -CWPU-1	58.50	219.97	45.04	125.22	36.03	2.94	57.1	65	little sedimentation	66.8
CO ₂ -CWPU-2	58.50	219.97	54.12	116.00	43.30	3.52	52.1	148	No sedimentation	104.48
CO ₂ -CWPU-3	58.50	219.97	62.10	108.11	49.68	4.03	41.6	152	No sedimentation	160
CO ₂ -CWPU-4	58.50	219.97	70.08	100.10	56.06	4.55	29.6	155	No sedimentation	225.33
CO ₂ -CWPU-5	58.50	219.97	89.66	80.56	71.73	5.80	25.3	175	No sedimentation	173.22
CO ₂ -CWPU-6	58.50	219.97	130.17	40.00	104.14	8.37	22.6	180	No sedimentation	30.37
PBA-CWPU-1	58.50	219.97	62.10	108.11	49.68	4.03	35.6	810	Much sedimentation	52.40
PBA-CWPU-2	58.50	219.97	70.08	100.10	56.06	4.55	31.7	960	Much sedimentation	63.50
PBA-CWPU-3	58.50	219.97	89.66	80.56	71.73	5.80	28.6	1300	No sedimentation	87.55



Scheme 1 Schematic illustration of the synthetic route to CO₂-CWPU.

CO₂-CWPU, CO₂-CWPU with MDEA contents as 2.94%, 3.52%, 4.03%, 4.55%, 5.80%, 8.37% were synthesized, named as CO₂-CWPU-1–CO₂-CWPU-6, respectively (Table 1). To embody the advantage of CO₂-polyols in improving properties of WPU, control samples using PBA as soft segments were also prepared, which were assigned as PBA-CWPU-1-3 with MDEA content as 4.03%, 4.55% and 5.80%, respectively.

The chemical structures of typical CO₂-polyol and CO₂-CWPU were investigated by FTIR and ¹H-NMR analysis using CO₂-CWPU-2. As shown in Fig. 1 (down), the infrared absorption bands at 1747 and 1251 cm⁻¹ are assigned to C=O and

C–O in carbonate group, and those at 2982, 2939, 2880, 1455 and 1380 cm⁻¹ are corresponded to CH₃, CH₂, and CH in the CO₂-polyol. Meanwhile the band at 1160 cm⁻¹ is ascribed to the ether group, and the broad band from 3475 cm⁻¹ to 3543 cm⁻¹ indicated the existence of OH. FTIR spectrum clearly demonstrates the characteristic structure of CO₂-polyol. Further, the presence of stretching vibrations of N–H at 3336 cm⁻¹ and blending mode of N–H at 1533 cm⁻¹ associated with the disappearance of the NCO vibration at 2274 cm⁻¹ demonstrated that OH reacted with NCO to afford urethane group. In addition, the appearance of characteristic

absorption bands belonged to CO₂-polyol in PU suggested the formation of CO₂-CWPU.

¹H-NMR spectra of CO₂-polyol and CO₂-CWPU are shown in Fig. 2, where CO₂-CWPU-2 was used as sample of CO₂-CWPU. According to the ¹H-NMR spectrum shown in Fig. 2(A), typical proton signals belonged to IPDI at 0.79–0.93 ppm (methyl protons) and 0.93–1.11 ppm (methylene protons) indicated the reaction of IPDI and OH groups. As shown in Fig. 2(B), the signals of CO₂-polyol at 4.8–5.0 ppm and 3.9–4.3 ppm are assigned to CH and CH₂ groups in carbonate unit, and those at 3.3–3.7 ppm are assigned to CH and CH₂ groups in the ether unit. The signals at 8.11 ppm belongs to aromatic protons in PTA, demonstrating the successful incorporation of PTA in CO₂-polyol, which is of key importance to control the molecular weight. Collectively, both FTIR and ¹H-NMR spectra show the successful preparation of CO₂-polyol and CO₂-CWPU.^[39]

Effect of MDEA Content on Emulsion Particle Size, PSD, Solid Content, Viscosity and T_g

After the emulsification of CO₂-CWPU, the effect of MDEA content on the particle size, PSD, solid content and viscosity were explored. As shown in Figs. 3(a)–3(c), with an increase of MDEA content from 2.94% to 3.52% and then to 4.03%, samples CO₂-CWPU-1-3 all displayed unimodal PSD. Moreover, the particle size and PSD of CO₂-CWPU emulsion decreased with the increasing MDEA content, owing to the higher hydrophilic group allowed the formation of more ionic centers by quaternization in polyurethane chains. Interestingly, CO₂-CWPU-4 and CO₂-CWPU-5 with further enhanced MDEA (4.55% and 5.80%, respectively) exhibited bimodal PSD while CO₂-CWPU-6 with the value of 8.37% returned to single PSD (Figs. 3d–3f). It can be deduced that the particle size of WPU decreases with the increase of the MDEA content, as MDEA inhibited the fragmentation of the polymer into larger particles during the dispersion process. The change of unimodal or bimodal PSD

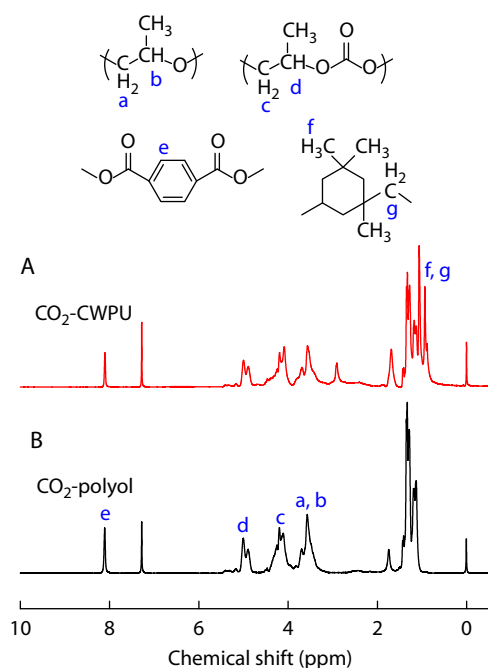


Fig. 2 ¹H-NMR spectra of (A) CO₂-CWPU and (B) CO₂-polyol.

with different MDEA content was caused by the hydrophilic property of CO₂-CWPU emulsion. Hydrophobic structural polyurethanes were obtained with lower MDEA content below 4.03%, then those strong hydrophobic segments wrapped up together and formed homogeneous large particles during water disperses, and thus unimodal PSD was found. As the MDEA content continue increasing to 5.80%, some better hydrophilic structural polyurethanes could be obtained, where these hydrophilic groups tended to locate on the particle surface by migrating toward the aqueous phase during the formation of particles and showed inhomogeneity, thus both large and small particles were formed and bimodal PSD was found. When the MDEA content further increased to 8.37%, the sufficient hydrophilic assured the formation of single distributed small particle excellent water-solubility polyurethanes and formed unimodal PSD. Therefore, the content of MDEA played an important role in determining the particle size and PSD of the CO₂-CWPU. The morphology of emulsions particles, were studied by transmission electron micrograph (TEM). As shown in Fig. 4(a), CO₂-CWPU-4 presents bimodal PSD with large globular particles centered on 135 nm while small particles around 40 nm. In addition, CO₂-CWPU-6 exhibits unimodal PSD with particle sizes around 35 nm to 60 nm. The emulsion appearance of CO₂-CWPU changed slowly from milky white to transparent with the increasing MDEA content (shown in Fig. S1, see the electronic supplementary information, ESI). It indicated that the increasing MDEA decreased the latex particle sizes and this tendency is agreed with the above result.

The incorporation of positive MDEA units can be utilized to synthesize CO₂-CWPU emulsion with high solid content yet low viscosity. As shown in Table 1, CO₂-CWPU-1 with MDEA content of 2.94% displays a high solid content of 57.1 wt% and an extremely low viscosity of 65 cps, which was attributed to partial sedimentation of the emulsion. With the increase of MDEA content, CO₂-CWPU-2-6 displayed no sedimentation with a slightly increased viscosity, which can be attributed to the augment of water swelling layer induced by the increment of total surface area of particles. Whereas, the solid content of the emulsion decreased progressively from 57.1% to 22.6% with an increase of MDEA content from 2.94% to 8.37%. Notably, CO₂-CWPU-2 displays not only a high solid content (52.1%) but also a low viscosity (148 cps), demonstrating the success of present molecular design.

From the DSC traces of CO₂-CWPU-1-6, depicted in Fig. 5, it can be seen that the glass transition temperature (T_g) of polyurethane increased from −3.75° C to 6.81° C with the increasing MDEA contents from 2.94% to 8.37%. The growth trend of T_g was caused by the growing hard segment content composed of MDEA.

Mechanical Performance of CO₂-CWPU

The tensile stress-strain curves of CO₂-CWPU with different contents of MDEA were studied. As shown in Fig. 6, with an increasing of MDEA content, the tensile strength (σ_m) of CO₂-CWPU increases while the elongation at break (ε_b) decreases. For example, the σ_m of CO₂-CWPU-1 reaches 16.27 MPa, which is lower than that of CO₂-CWPU-6 (32.17 MPa). Meanwhile the ε_b of CO₂-CWPU-1 is 433.67% much higher than that of CO₂-CWPU-6 (303.57%). These results indicated that more rigid N-MDEA group may increase the rigidity leading to decreased elongation

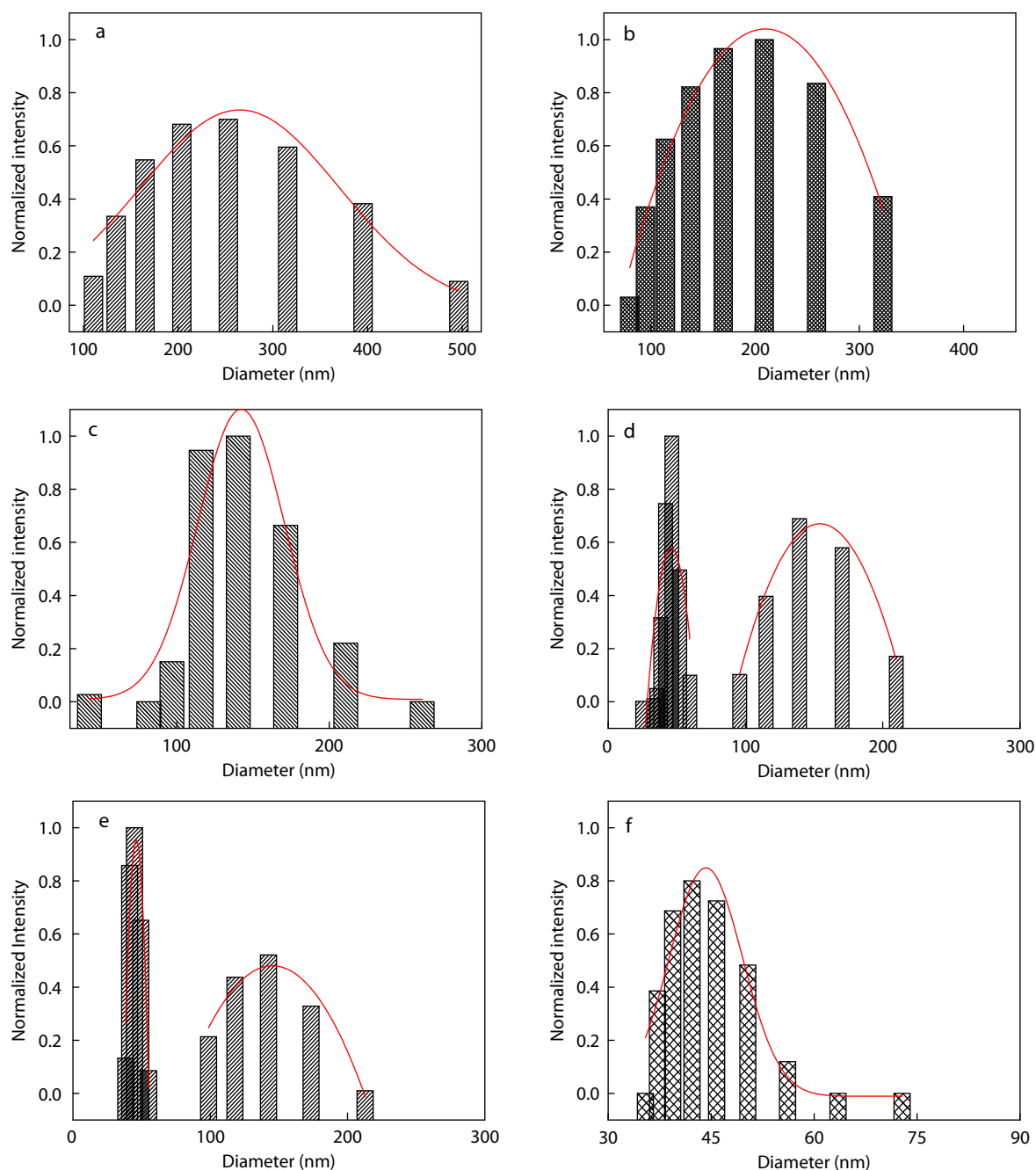


Fig. 3 Particle size distribution of CO₂-CWPU: (a) CO₂-CWPU-1, (b) CO₂-CWPU-2, (c) CO₂-CWPU-3, (d) CO₂-CWPU-4, (e) CO₂-CWPU-5 and (f) CO₂-CWPU-6.

at break.

T-peel Strength Tests

T-peel strength of adhesive bonds of CO₂-CWPU was determined (Table 1). The T-peel strength of CO₂-CWPU-1 containing 2.94% of MDEA is very low (66.8 N/5cm). At low ionic center concentrations, the effective Coulombic forces and H-bonding from hard segments (MDEA) are much weak for bonding two surfaces together. The bond strengths increased from 104.48 N/5cm to 160 N/5cm then to 225.33 N/5cm with increment of ionic centers from 3.52% to 4.03% and then to 4.55%. CO₂-CWPU-4 with 4.55 wt% N-MDEA shows the highest

adhesion strength of 225.33 N/5cm. It indicated that better adhesion was achieved when more Coulombic attraction forces were available among the ionic center sites in these cases.

However, lower adhesion strengths were obtained with a further increase in the ionic center sites (MDEA contents of 5.8%–8.3%). It was believed that even at a higher percentage of ionic sites in the polymeric backbone, the ionomeric chain might prefer to be in an ionic cluster structure. Moreover, with the increment in the ionic centers, the hydrophilicity of the polymer increased significantly, which, in turn, increased the plasticization and the tackiness. Thus, it resulted in lower

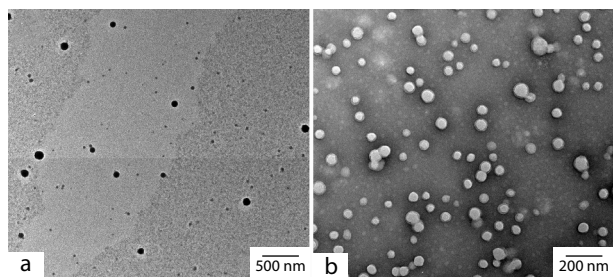


Fig. 4 TEM images of (a) CO₂-CWPU-4 and (b) CO₂-CWPU-6.

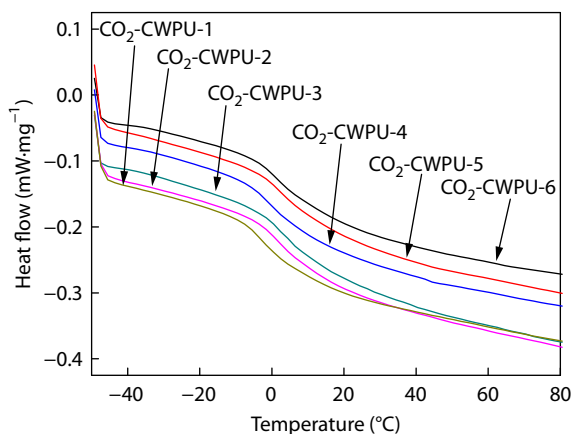


Fig. 5 DSC curves of CO₂-CWPU-1 to CO₂-CWPU-6 with different contents of MDEA.

bond strength.

T-peel strength of adhesive bonds of PBA-WPU was also determined (Table 1). It was observed that PBA-WPU had a lower T-peel strength (87.55 N/5cm) compared with CO₂-WPU (173.22 N/5cm) under same MDEA content (5.8%). The higher T-peel strength obtained from CO₂-WPU compared with PBA-WPU was believed to be due to the presence of enhanced hydrogen bonding and the synergistic improvement of soft segment and hard segment. The hydrogen-bonding interaction between soft segment and hard segment was investigated by

the FTIR technique. The hydrogen bonded N—H stretching (3336 cm⁻¹) in CO₂-CWPU (shown in Fig. 1) blue-shifted compared to that of PBA-CWPU (3368 cm⁻¹) (Fig. S2, in ESI), indicating an increase in the average strength of the hydrogen bonds.^[33] Therefore the intensity of hydrogen bonded N—H order was as follows: CO₂-WPU>PBA-WPU. The band of CO₂-CWPU around 1749 cm⁻¹ broadened and a new band appeared and became distinguishable at shoulder band of 1710 cm⁻¹ that was typically assigned to the hydrogen-bonded carbonyl of CO₂-polyols.^[41] The much more hydrogen bonding of CO₂-CWPU than that of PBA-WPU was caused by the structure of CO₂-polyols, in which ether unit can also form hydrogen bonding except of carbonate group. As discussed above, MDEAs as strongly polar cationic groups incorporated into the backbone of CWPU considerably improved polarity and intermolecular forces within those segments.^[37] Therefore, the synergistic improvement of soft segment (CO₂-polyols) and hard segment (MDEA) imparted the CO₂-CWPU which provide more oxygen atom involved in hydrogen excellent adhesion.

Water Absorption/Hydrolysis/Oxidation Resistance

The water absorption, hydrolysis and oxidation resistance of CO₂-CWPU films were studied using PBA-CWPU films as control. The appearance changes of CO₂-CWPU-2 and PBA-CWPU-3 films with different immersion time in deionized water were shown in Fig. S3 (in ESI). It can be seen that no obvious changes for CO₂-CWPU-2 films with the increasing immersion time, whereas PBA-CWPU-3 films dramatically swelled within 30 min and then the swelling became more and more serious with extended soaking time. As shown in Fig. 7(a), the water absorption of PBA-WPU film reaches 17.6% after immersing for 30 min though its length showed almost no change. With continuous immersion, the film swelled dramatically and became flat after immersing for 120 min, meanwhile, its water absorption was saturated (76.70%). Fig. 7(b) shows that the PBA-WPU film swelled to 76.70% after 120 min and then maintains at this value despite continuous immersion. Compared with PBA-CWPU, CO₂-CWPU film shows better water absorption resistances. Its water absorption is only 10.72% after immersing 120 min and then maintained at this saturated value. From what

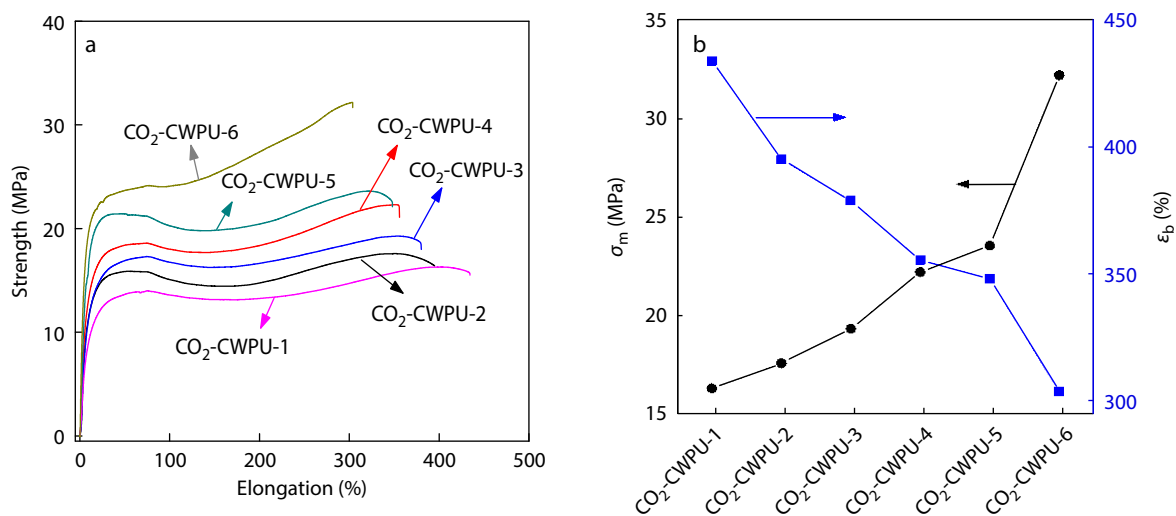


Fig. 6 (a) Tensile stress-strain curves of CO₂-CWPU-1 to CO₂-CWPU-6 with different contents of MDEA; (b) The variations of σ_m and ϵ_b .

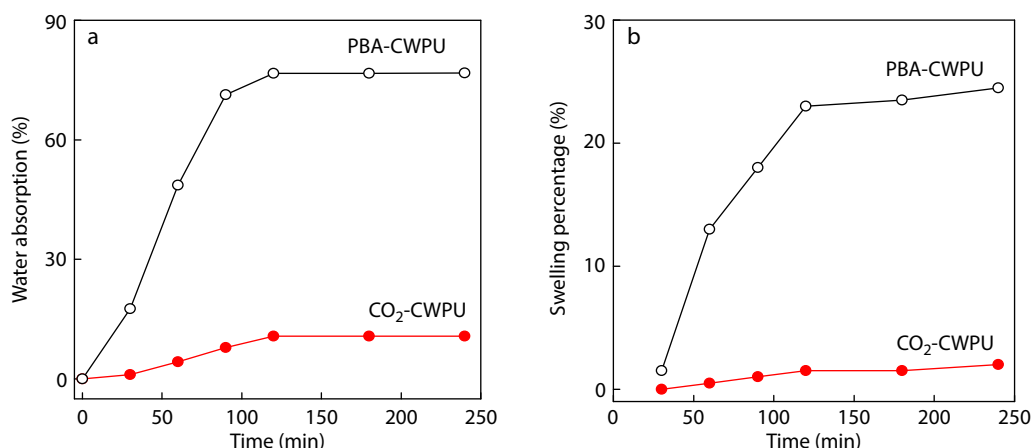


Fig. 7 Behavior of CO₂-CWPU-2 and PBA-CWPU-3 films in H₂O (a) water absorption and (b) swelling percentage.

has been discussed above, The CO₂-CWPU film showed excellent resistance against water swelling and its swelling percentage was only 2% after immersing 240 min. The estimation of hydrolysis resistances for CWPU films was investigated by monitoring the changes of the film surface in Fig. S4 (in ESI) with immersion time after soaking in 5% NaOH solution at 25 °C. As shown in Fig. S3 (in ESI), the PBA-CWPU films changed from transparent to white and with distinct swelling then turned severely softened after immersion in NaOH solution, whereas, no any changes were found for the CO₂-CWPU. To further study the appearance change of the films, the digital microscope was used and shown in Fig. 8. It is interesting to note that no obvious apparent change for CO₂-CWPU film (Fig. 8c), however, PBA-CWPU film was eroded severely and lots of potholes were produced on the surface (Fig. 8d) after 4-time immersions in NaOH solution. The defect of PBA-CWPU film was caused by its poor hydrolysis/oxidation resistance, in which the sodium hydroxide could easily permeate the film and then formed crystal, whereas, CO₂-CWPU film can prevent the penetration of alkaline solution. The hydrolysis/oxidation resistance of CO₂-CWPU-2 and PBA-CWPU-3 films was also investigated by monitoring the changes in tensile strength with immersion time after soaking in 5% NaOH solution and 10% H₂O₂ at 25 °C, respectively. As shown in Fig. 9(a), the retention strength for CO₂-CWPU film reached 96.5% after immersing 240 min in NaOH solution, no obvious change with continuous immersing

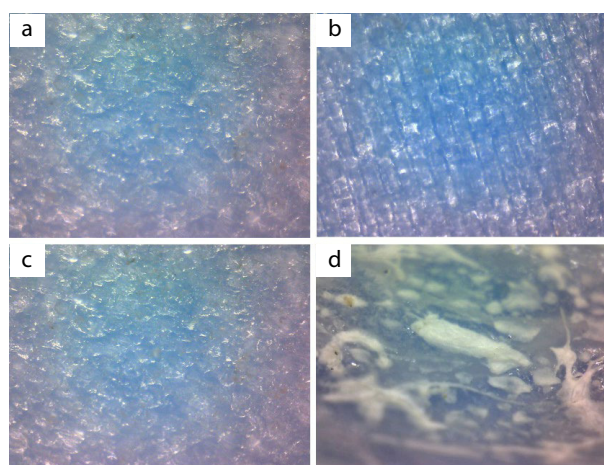


Fig. 8 Photographs for Images of CO₂-CWPU-2 (a, c) and PBA-CWPU-3 films (b, d) on the immersion in a 5% NaOH solution: (a, b) before immersion, (c, d) after 4 h immersion (magnified 500 times).

480 min and a 91.2% retention strength was obtained. Compared with CO₂-CWPU film, PBA-CWPU film showed poor hydrolysis resistances, in which the retention strength of PBA-CWPU film dropped quickly to 32% after 240 min and its mechanical properties were lost after 360 min. Like the hydrolysis tendency, CO₂-CWPU gave better result after

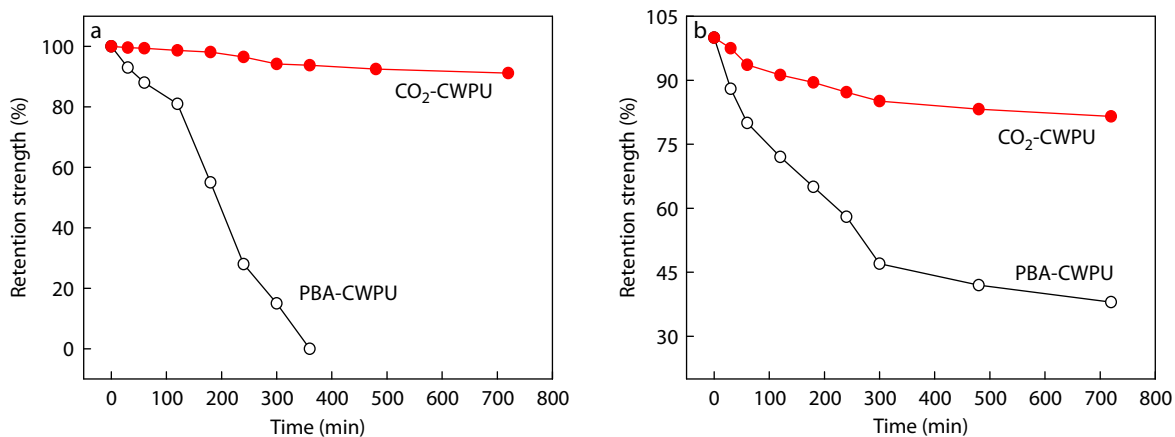


Fig. 9 Retention strength for CO₂-CWPU-2 and PBA-CWPU-3 films in (a) 5% NaOH solution (b) and 10% H₂O₂.

immersion in 10% H₂O₂ solution. It was noting from Fig. 9(b) that the CO₂-CWPU film showed a retention strength of 81.5% after 720 h immersion, while that of PBA-CWPU film dropped to 38%, indicating that CO₂-CWPU had excellent oxidation resistance compared with PBA-CWPU.

The superior water absorption and hydrolysis/oxidation resistances of CO₂-CWPU films than those of PBA-CWPU may be due to their good hydrolysis resistance of carbonate and ether moieties in the soft segment from backbone. Collectively, CO₂-CWPU-2 showed a high solid content of 52%, a low viscosity (148 cps), strong T-peel strength (104 N/5cm) and excellent ageing resistance, which provides a new platform for designing excellent WPU materials.

CONCLUSIONS

A series of CO₂-CWPU were successfully synthesized with different content of MDEA. In particular, CO₂-CWPU-2 with stable aqueous dispersion with 52% solid content was obtained even MDEA loading was as low as 3.52 mol%. The mechanical performance of the cationic CO₂-CWPU film can be adjusted by the MDEA loading. CO₂-CWPU play a major role due to their better adhesion compared with PBA-CWPU in the field of cationic waterborne adhesives. In addition, CO₂-CWPU showed much better hydrolysis/oxidation resistance than PBA-CWPU due to the coexistence of carbonate units and ether units in one CO₂-polyol molecule.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2738-9>.

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