Transformation of Commodity Poly(hydroxyether of bisphenol A) into Vitrimers via Post Crosslinking with Hindered Urea Bonds

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Abstract In this contribution, we reported the preparation of vitrimers by using commodity thermoplastics via post crosslinking with hindered urea bonds (HUBs). First, three hindered urea diisocyanates (HUDIs) were synthesized via the reactions of N,N′-di-tert-butylethylenediamine, N,N′-diethylethylenediamine, and piperazine with isophorone diisocyanate (IPDI). Thereafter, these HUDIs were used as the crosslinking agents to crosslink poly(hydroxyether of bisphenol A) (PH), a commodity thermoplastic. Fourier transform infrared (FTIR) spectroscopy and dynamic mechanical thermal analyses (DMTA) indicated that the PH thermosets were successfully obtained. It was found that the thermosets displayed the behavior of vitrimers. The PH thermosets can be reprocessed at elevated temperature without using catalyst and the mechanical strengths of vitrimers were recovered as high as 95%. The reprocessing properties are attributable to dynamic exchange reaction of hindered urea bonds, contingent on types of hindered urea bonds.

Keywords Vitrimer; Poly(hydroxyether of bisphenol A); Hindered urea bonds; Reprocessing properties

INTRODUCTION

In terms of processing properties, glassy polymers can be categorized into thermoplastics and thermosets. With linear (or branched) structures, thermoplastics are readily moulded in melts at elevated temperature, displaying excellent reprocess (or recycling) properties. In contrast, thermosets can only be moulded in the form of malleable monomers (or precursors), which are then vitrified via subsequent curing reaction (or polymerization). With curing reaction, sol-gel transitions occur and the systems are transformed into crosslinked networks. It is the formation of crosslinked networks that endow thermosets with excellent thermomechanical strength and chemical resistance, which are irreplaceable for application of thermosets as structural materials. Due to formation of static crosslinked networks, however, thermosets can no longer be reprocessed (or and recycled). It is desirable to develop glassy polymers combining the advantages of both thermoplastics and thermosets. Leibler et al.[1] proposed a concept of „vitrimer”. Vitrimers are a class of crosslinked polymer networks containing dynamic bonds. Their reprocessing can be achieved via the exchange of the dynamic bonds. At service temperature, vitrimers behave as conventional thermosets. Nonetheless, the exchanges of dynamic bonds can be triggered at elevated temperatures. As a consequence, the thermosets display weldability, thermal plasticity, or malleability. With dynamic covalent bonds, these thermosets are referred to as covalent adaptable networks (CANs). According to the exchange mechanism of dynamic bonds, CANs can be divided into (i) dissociative and (ii) associative types. In dissociative CANs, exchanges of dynamic bonds are based on equilibrium of reaction between reactants and products, which are highly temperature-dependent; the reprocessing is carried out via sol-gel transition of system at certain temperature. As one of the typical dissociative dynamic chemistries, Diels-Alder reaction has been employed to obtain CANs.[2–5] In 2011, Leibler et al.[1] reported that dynamic exchange was performed via transesterification in epoxy thermosets cured with acid or and anhydride. The reprocessing of thermosets is achieved in an associative manner and no de-crosslinking reaction occurs. The similar mechanism was also found in other vitrimers based on disulfide metathesis,[6–10] trithiocarbonate exchange,[11] tricarbamoyleation of polyurethanes and polyhydroxyurethanes,[12,13] poly(oxime-urethanes),[14] transamination exchange reactions,[15] transamination of vinylogous amides or urethanes,[16] and imine exchange of polyimines.[17] To fulfil the exchange of dynamic bonds, catalysts are generally required to incorporate into systems.[18] Recently, Cheng et al.[19] reported that polyurethane elastomers were endowed with self-healing properties after hindered urea bonds (HUBs) were introduced. It is of interest to utilize HUBs to

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prepare catalyst-free vitrimers with high glass transition temperatures ($T_g$’s).

Vitrimers can be prepared via curing (or polymerization) reaction of small molecule precursors (or monomers). In addition, vitrimers can be obtained via post crosslinking of existing thermoplastics. It is attractive to transform existing commodity thermoplastics into vitrimers by using commercially available and inexpensive reagents. Recently, Nicolay and Leible$^{[25]}$ reported the modification of several commodity polymers with carbon-carbon backbones into high-performance vitrimers via dioxaborolane metathesis. Chen and Manas-Zloczower$^{[26,27]}$ obtained recycled poly(ethylene-vinyl acetate) viotrimers by introducing the crosslinking points of triethyl borate. By adding 1,5,7-triazabicyclo[4.4.0]dec-5-ene, a transesterification catalyst, Zhu et al.$^{[28]}$ converted poly(ethylene-co-vinyl acetate) into dynamic covalent networks. However, such an investigation remains largely unexplored.

In this communication, we reported the preparation of the vitrimers based on poly(hydroxyether of bisphenol A) (PH), a commodity thermoplastics. PH was first developed by Union Carbide Plastics Co. in 1960’s under the trade name of Phenox$^{[29]}$ and it has been widely applied as thermoplastics and coating materials. PH can be synthesized via polycondensation of bisphenol A and epichlorohydrin or polyaddition of diglycidyl ether of bisphenol A with bisphenol A.$^{[30]}$ In this work, we explored to post-crosslink PH with hindered urea diisocyanates (HUDs) (Scheme 1). Owing to the introduction of hindered urea bonds (HUBs), the PH vitrimers are expected to exhibit reprocessing (or recycling) properties. To the best of our knowledge, there has been no previous report on the transformation of PH into vitrimers.

**EXPERIMENTAL**

**Materials**

Poly(hydroxyether of bisphenol A) (PH) was supplied by Shanghai Reagent Co., China and it had the molecular weight of $M_n = 5.57 \times 10^4$ with $M_w/M_n = 1.92$. N,N’-di-tert-butylethlenediane (DBDA), N,N’-diethylthelenediamine (DEDA), and piperazine (PAZ) were of analytical pure grade and purchased from TCI Co., China. Isophorone diisocyanate (IPDI) and dibutyltin dilaurate were purchased from Adamas Co., Shanghai, China.

**Synthesis of Hindered Urea Diisocyanates**

Typically, IPDI (444.6 g, 2.0 mol) and anhydrous N,N’-dimethylformamide (DMF, 100 mL) were added to a flask with stirring. At 0 °C, N,N’-di-tert-butylethlenediamine (DBDA) (172.32 g, 1.0 mol) dissolved in DMF (500 mL) was slowly added to the flask. The reaction was carried out at room temperature overnight. The majority of solvent was removed via rotary evaporation and the residual solvent was eliminated in vacuo at 70 °C for 72 h. The product (viz. di-t-tert-butylethylene urea diisocyanate, DBDA-IPDI) (586.2 g) was obtained with the yield of 95%. Both N,N’-diethylthelenediamine (DEDA) and piperazine (PAZ) urea disiocyanates were synthesized by following the similar procedure.

$^1$H-NMR of DBDA-IPDI (DMSO-d$_6$, $\delta$, ppm): 6−5.4 [2H, NH], 3.78−3.57 [2H, $\text{CH}_2\text{NH}$, $\text{CH}_2\text{NCO}$], 3.43–3.20 [8H, $\text{CH}_2\text{NCO}$, $\text{CH}_2\text{NH}$, $\text{NCH}_2\text{CH}_2\text{N}$], 1.64–1.40 [4H, $\text{CH}_2\text{C}(\text{CH}_2)_2\text{CH}_2$], 1.40−1.16 [26H, $\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})_2$], 1.0−0.6 [18H, C($\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N}$)], $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})$, $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})]$. $^1$H-NMR of DEDA-IPDI (DMSO-d$_6$, $\delta$, ppm): 6.54−5.95 [2H, NH], 3.92−3.50 [2H, $\text{CH}_2\text{NH}$, $\text{CH}_2\text{NCO}$], 3.34−3.04 [12H, $\text{CH}_2\text{NH}$, $\text{NCH}_2\text{CH}_2\text{N}$], 1.77−1.56 [4H, $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})_2$], 1.56−1.27 [8H, $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})_2$], 1.27−0.6 [18H, C($\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N}$)], $\text{C}(\text{CH}_2\text{NHCH}_2\text{N})$, $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})_2$]. $^1$H-NMR of PAZ-IPDI (DMSO-d$_6$, $\delta$, ppm): 6.54−6.11 [2H, NH], 3.92−3.50 [2H, $\text{CH}_2\text{NH}$, $\text{CH}_2\text{NCO}$], 3.47−3.04 [12H, $\text{CH}_2\text{NH}$, $\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}$], 1.68−1.34 [4H, $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})_2$], 1.34−1.15 [8H, $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})_2$], $\text{Ni(CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N})$, $\text{CH}_2\text{C}(\text{CH}_2\text{NCOCH}_2\text{CH}_2\text{N})_2$].

**Preparation of PH-HUB Vitrimers**

First, PH was dissolved in a possibly small amount of DMF and then equimolar hindered urea diisocyanate with respect to PH was added to a solution of HUBs. The reaction mixture was heated at 80 °C for seven days and then filtered. The resulting PH-HUB vitrimer (Scheme 1) was recovered and dried in vacuo at 70 °C for 48 h.

![Scheme 1](https://doi.org/10.1007/s10118-020-2457-z)
hydroxyl groups of PH was added to the solution with vigorous stirring. The reaction was performed at 110 °C for 4 h with dibutyltin dilaurate (DBTDL) as the catalyst. With the reaction proceeding, notably, the system was gradually gelled. The majority of solvent was evaporated at 70 °C overnight and the residual solvent was in vacuo eliminated at 60 °C for two weeks. The sample was then hot-pressed into a monolith at 150 °C.

**RESULTS AND DISCUSSION**

Hindered urea disiocyanates (HUDIs) were synthesized via the reaction of isophorone disiocyanate (IPDI) with three hindered diamines, i.e., N,N'-di-tert-butylhexylenediisocyanate (DBDAO), N,N'-diethylhexylenediisocyanate (DEDA), and piperazine (PAZ) as shown in Scheme S1 (in the electronic supplementary information, ESI).

In the reaction, the hindered diamines dissolved in DMF were slowly added to the solutions of IPDI. The reacted products were subjected to Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. The FTIR spectra are shown in Fig. S1 (in ESI). The broad bands displayed in the range of 3000−3800 cm⁻¹ are assignable to the stretching vibration of N−H bonds in carbamate moieties. In the meantime, the bands at 2264 cm⁻¹ are characteristic of the stretching vibration of isocyanate groups; the intense bands at 1660 cm⁻¹ are assignable to the stretching vibration of urea bonds. The FTIR spectroscopy indicates that the products combined the structural features from IPDI and the hindered diamines. The structures were further investigated by means of NMR spectroscopy as shown in Fig. S2 (in ESI). Notably, the signals of resonance from IPDI and the corresponding diamines were simultaneously detected. All the as-obtained HUDIs were subjected to gel permeation chromatography (GPC) and the GPC curves are shown in Fig. S3 (in ESI). Notably, all the products displayed peaks with the retention time of ca. tᵣ = 28 min, which were quite close to the position of the marker (viz. DMF eluent). FTIR, 'H-NMR, and GPC results indicate that the HUDIs were in reality the isocyanate-terminated telechelics with low molecular weights.

The HUDIs were used to crosslink PH via the reaction of hydroxyls of PH with isocyanate groups of HUDIs. After the reaction, notably, the reacted products were no longer soluble in common solvents such as tetrahydrofuran, chloroform, and DMF, in marked contrast to plain PH. This observation indicates the crosslinked structures were formed in these products, i.e., the PH-HUB thermosets were obtained. The PH-HUB thermosets were subjected to FTIR spectroscopy and the FTIR spectra are shown in Fig. 1. It is seen that all the samples displayed the broad bands in the range of 3000−4000 cm⁻¹. For PH, the broad band centred at 3396 cm⁻¹ is assignable to the stretching vibration of hydrogen-bonded hydroxyl groups. After crosslinking of PH with HUDIs, the band shifts to lower wavenumbers at 3337−3330 cm⁻¹. The bands at the lower wavenumbers are assignable to the stretching vibration of N−H in carbamate groups, which were generated from the reaction of isocyanate groups with hydroxyl groups.

This reaction was completed as indicated by the disappearance of the bands at 2264 cm⁻¹. The carbamate groups in the thermosets can be further evidenced by the appearance of the bands at 1724 cm⁻¹ whereas the stretching vibration of urea bonds was detected at 1630 cm⁻¹.

The PH-HUB thermosets were subjected to dynamic mechanical thermal analysis (DMTA) and the DMTA curves are shown in Fig. 2. For PH, a major peak was detected at 102 °C, attributable to the glass transition of this polymer. For PH, rubbery plateau did not appear in the plot of storage modulus as a function of temperature. This observation can be explained in terms of (i) the linear structure and (ii) the fairly low molecular weight of PH sample. After crosslinked with HUDIs, however, the glass transitions were shifted to the higher temperatures, depending on the type of HUBs. For PH-HUB(DBDA), PH-HUB(DEDA), and PH-HUB(PAZ), the Tᵣ’s were measured to be 106, 117, and 118 °C, respectively. Under the identical condition, notably, all the PH-HUBs displayed the rubbery plateaus, which were stable until 200 °C or higher. The appearance of rubbery plateaus is indicative of the formation of crosslinked networks. It is seen that the PH-HUBs displayed the storage moduli (E') higher than that of PH. The increased Tᵣ's, E's, and the appearance of rubbery plateaus indicate that PH was virtually crosslinked, i.e., the PH-HUB ther-

**Fig. 1** FTIR spectra of (a) PH, (b) PH-HUB(DBDA), (c) PH-HUB(DEDA), and (d) PH-HUB(PAZ).

**Fig. 2** DMTA curves of (a) PH, (b) PH-HUB(DBDA), (c) PH-HUB(DEDA), and (d) PH-HUB(PAZ).
mosets were successfully obtained.

It is of interest to examine the reprocessing properties of the PH-HUBs. The thermosets were cut into small fragments, which were then hot-pressed at 180 °C (Fig. 3). Notably, the PH-HUB(DBDA) fragments were readily reprocessed into a monolith within 25 min. For PH-HUB(DEDA), the similar behavior was displayed but a longer time (e.g., 40 min) was required. For PH-HUB(PAZ), it was hard to obtain a good monolithic body even when the fragments were hot-pressed at 180 °C for 40 min or longer. The reprocessing behavior is attributable to the introduction of HUBs. It has been realized that HUBs are a class of dynamic covalent bonds. Owing to the addition of bulky groups to an amide nitrogen atom, the amide bond and the hindered urea bond will dissociate into isocyanate and amine. Nonetheless, isocyanate readily reacts with amine. As a consequence, the dissociation and association between isocyanate and amine groups frequently and reversibly occur. In the present case, the reprocessing properties of the thermosets are attributable to the introduction of HUBs. It should be pointed out that the control PH thermoset crosslinked with isophorone diisocyanate could not be reprocessed under the identical condition (Fig. S4 in ESI). At elevated temperature, the dynamic exchanges of HUBs took place, resulting in the recombination of broken chemical linkages in the crosslinked networks, i.e., the surfaces of fragments were welded. Notably, the reprocessing properties were quite dependent on the type of HUBs, which could reflect the difference in dynamic exchange ability of HUBs. To confirm this speculation, we investigated the solubility of the PH-HUBs in the solutions while the corresponding hindered amines were added. For PH-HUB(DBDA) and PH-HUB(DEDA) thermosets, full dissolution could be attained while DBDA and DEDA were respectively added to the systems (Fig. S5 in ESI). The re-dissolution behavior is attributable to the occurrence of exchange reaction among the HUBs. The externally added hindered diamines participated in the exchange reaction of HUBs, giving rise to the dismantlement of the inter-chain linkages (viz. HUBs). In this work, we recovered PH from the solutions by adding the precipitant (viz. methanol) and the as-obtained PH samples were further subjected to the GPC measurement (Fig. S6 in ESI). Notably, the recovered PH samples displayed the GPC curves very close to that of the pristine PH, indicating that the exchanges of dynamic covalent bonds only occurred in the HUBs other than the main chains of PH. For PH-HUB(PAZ), however, no redissolution was observed after piperazine was added even while the solution was held for one week, suggesting that the dynamic exchange of hindered urea bonds was very slow or hardly occurred. The exchange kinetics of HUBs would significantly influence the reprocessing properties of the PH-HUB thermosets, which was readily investigated by means of stress relaxation tests.

Also shown in Fig. 3 are the stress relaxation curves of the PH-HUBs. For PH-HUB(DBDA) and PH-HUB(DEDA), the stresses were readily relaxed to zero. For PH-BUD(PAZ), the stress could not be relaxed to zero even when the sample was annealed at 170 °C for 180 min. Assuming that the stress relaxation behavior resulted from the dynamic exchange of HUBs at elevated temperature, we can use the stress relaxation time (τ) (which is defined as the time at which stress is relaxed to 1/e of the initial stress) to estimate the activation energy of the exchange reaction according to an Arrhenius model:
where \( \tau \) is stress relaxation time, \( A \) is a pre-exponential factor, \( T \) is temperature, and \( R \) is gas constant. By using the plots of logarithm of \( \ln \tau \) as functions of \( 1/T \), the values of activation energy (viz. \( E_a \)) were calculated; the activation energies were obtained to be 104.2, 114.6, and 122.8 kJ·mol\(^{-1}\) for the HUB(DBDA), HUB(DEDA), and HUB(PAZ) thermosets, respectively. The values of activation energy indicate that the difficulty in reprocessing of thermosets increased from HUB(DBDA), HUB(DEDA), to HUB(PAZ) thermosets, respectively. This result is in good agreement with the self-healing properties of poly(urethane) elastomers as reported by Cheng et al.\(^{[24]} \) For hindered urea bonds, the kinetics of dynamic exchange is quite dependent on the equilibrium constants of exchange reactions \( (K_{eq} = k_r/k_i) \) and rate of inverse reaction \( (k_i) \). The intensive exchange reaction of hindered urea bonds generally requires large \( K_{eq} \) and \( k_i \), at the same time. Cheng et al.\(^{[24]} \) found that from high to low, both \( K_{eq} \) and \( k_i \) were in the order of HUB(DBDA), HUB(DEDA), and HUB(PAZ). To evaluate the recovery of mechanical properties, the original and reprocessed thermosets were subjected to the measurement of fracture toughness with three-point bending tests (Scheme S2 in ESI), which can give the flexural moduli \( (E) \) and critical stress intensity factors \( (K_{IC}) \). These two values are very sensitive to defects in the materials, which are directly related to the surface welding degrees of cut fragments in the thermosets. Shown in Fig. 4 are the plots of loading as functions of deflection and the plots of \( E \) and \( K_{IC} \) as functions of reprocessing numbers for PH-HUB(DBDA), PH-HUB(DEDA), and PH-HUB(PAZ) vitrimers. It is seen that all the as-obtained (denoted the first reprocessed) samples had the very similar \( E \) and \( K_{IC} \) values. After experiencing two and three times of reprocessing, notably, the \( E \) and \( K_{IC} \) values of PH-HUB(DBDA) thermosets were still close to those of the first reprocessed sample, indicating that the mechanical strength was almost completely recovered. For PH-HUB(DEDA), the \( E \) and \( K_{IC} \) values were abruptly decreased after the sample was reprocessed twice, suggesting that the recovery of mechanical strength of the thermoset was lower than that of PH-HUB(DBDA). The decreased properties suggest that the defects in materials were hardly welded with the short reprocessing time. If this speculation is true, the recovery of mechanical properties would be improved if the reprocessing process was prolonged. It is of interest to note that the \( E \) and \( K_{IC} \) values were indeed enhanced after the sample was reprocessed for a longer time, i.e., after the sample was reprocessed thrice. In marked contrast to PH-HUB(DBDA), and PH-HUB(DEDA), the \( E \) and \( K_{IC} \) values of PH-HUB(PAZ) monstrously decreased with increasing the number of reprocessing, indicating that under the identical condition the mechanical strength was hardly recovered owing to the slowest kinetics of the HUBs.

**CONCLUSIONS**

In summary, hindered urea disocyanates (HUDIs) were synthesized via the reaction of isophorone diisocyanate (IPDI) with \( NN' \)-di-tert-butylenediamine, piperazine, and \( NN' \)-diethylhexylenediamine. These HUDIs were used as the crosslinking agents to prepare PH-HUB thermosets. The PH-HUB thermosets displayed the behavior of vitrimers, i.e., the thermosets can be reprocessed at elevated temperature without using catalyst. The reprocessing properties of the vitrimers were quite contingent on the type of hindered urea bonds, which was demonstrated with dynamic exchange kinetics of the HUBs and the measurements of mechanical properties. By introducing the HUBs based on \( NN' \)-di-tert-butylenediamine and \( NN' \)-diethylhexylenediamine, the vitrimers can display the recovery of mechanical strength as high as 90%.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at [https://doi.org/10.1007/s10118-020-2457-z](https://doi.org/10.1007/s10118-020-2457-z).

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