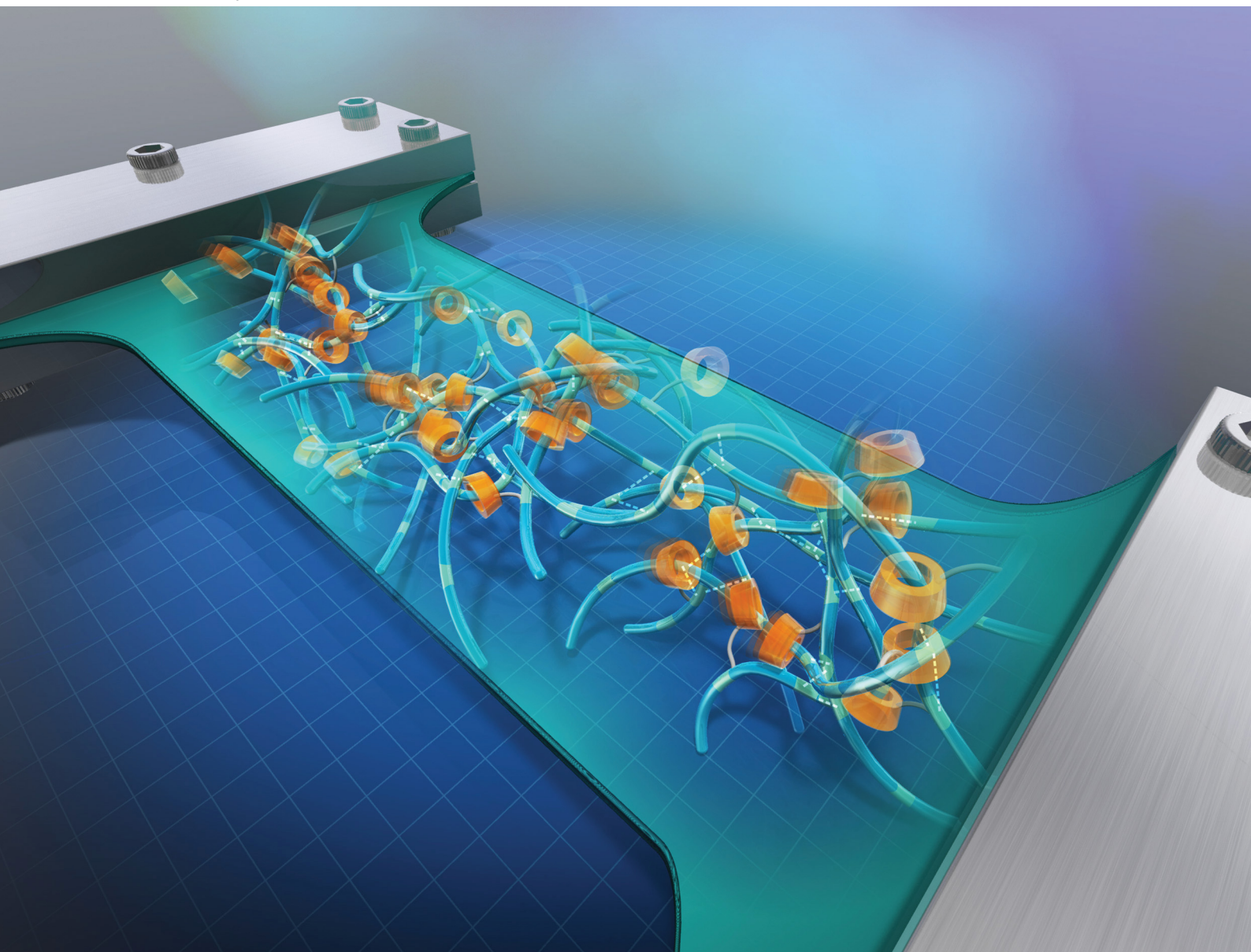


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Synergetic improvement in the mechanical properties of polyurethanes with movable crosslinking and hydrogen bonds†

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Polyurethane (PU) materials with movable crosslinking were prepared by a typical two-step synthetic process using an acetylated γ -cyclodextrin (TAc γ CD) diol compound. The soft segment of PU is polytetrahydrofuran (PTHF), and the hard segment consists of hexamethylene diisocyanate (HDI) and 1,3-propylene glycol (POD). The synthesized PU materials exhibited the typical mechanical characteristics of a movable crosslinking network, and the presence of hydrogen bonds from the urethane bonds resulted in a synergistic effect. Two kinds of noncovalent bond crosslinking increased the Young's modulus of the material without affecting its toughness. Fourier transform infrared spectroscopy and X-ray scattering measurements were performed to analyze the effect of introducing movable crosslinking on the internal hydrogen bond and the microphase separation structure of PU, and the results showed that the carbonyl groups on TAc γ CD could form hydrogen bonds with the PU chains and that the introduction of movable crosslinking weakened the hydrogen bonds between the hard segments of PU. When stretched, the movable crosslinking of the PU materials suppressed the orientation of polymer chains (shish-kebab orientation) in the tensile direction. The mechanical properties of the movable crosslinked PU materials show promise for future application in the industrial field.

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1. Introduction

In recent years, research on polymer elastomers has received increasing attention and has had an irreplaceable effect on many fields, especially regarding wearable devices,^{1–3} flexible robots,^{4–6} and responsive materials.^{7–9} The applications of polymer elastomers are closely related to their mechanical properties. Therefore, many methods have been used to improve the mechanical properties of elastomers, such as adding fillers,^{10–13} polymer blending,^{14–16} minimizing structural defects^{17,18} and introducing a crosslinking network with reversible covalent^{19–21} or noncovalent bonds (such as hydrogen bonds,^{22–32} metal coordination bonds,^{33–36} π - π stacking,^{37–39} ionic interactions,^{40–43} and host-guest complexes^{44–53}). However, it is still a challenge to fabricate a polymer with high toughness and a high Young's modulus (E) simultaneously.

Previously, our group prepared movable crosslinking elastomers (called single movable cross-network (SC) elastomers) using acrylate-based or acrylamide-based polymers as polymer main chains.^{53,54} SC elastomers have higher toughness than chemically crosslinked elastomers due to their unique movable crosslinking structures. However, because the toughness and

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Young's modulus of a material are essentially contradictory properties, the preparation of elastomers with a high modulus as well as high toughness based on SC elastomer design remains a challenge. Adjusting the main-chain polymer type, as well as regulating the crosslinking density, is very useful for controlling the E of SC elastomers.

Herein, we successfully prepared polyurethane (PU) elastomers containing movable crosslinking based on the design of SC elastomers. We used PU as the main chain, and the physical crosslinking formed by the abundant hydrogen bond interactions in PU synergistically interacted with the introduced cyclodextrin (CD) movable crosslinker. Our design enables the modification of polyurethane networks using inexpensive modified CDs without the addition of other compounds. Compared to other designs that directly introduced β CD into PU,^{55,56} the PU prepared in this work formed movable crosslinks. The PU materials with movable crosslinking had higher E values than the linear PU elastomer without crosslinking (LPU) as well as the chemically crosslinked PU elastomer with no decrease in toughness.

2. Results and discussion

2.1. Preparation of PUs with movable crosslinking

Fig. 1(a) shows the structural formula of PUs with movable crosslinking introduced by acetylated γ -cyclodextrin (TAc γ CD) (γ CDMe(x)PU), where x refers to mol% of crosslinking (here TAc γ CD), prepared by a two-step polymerization method (Scheme S2 and Table S1, ESI†). Dried TAc γ CD diol monomer (Scheme S1 and Fig. S1–S3, ESI†) and poly(tetrahydrofuran) (PTHF; $M_n = 1000$) were first mixed in dichloromethane (DCM). Then, excess hexamethylene diisocyanate (HDI) and dibutyltin-diacetate (DBTDA) were added to the DCM solution for pre-polymerization to obtain isocyanate-terminated chains. Subsequently, the chains were expanded by the addition of a diol chain extender, propan-1,3-diol (POD), at 25 °C. The polymerization reaction was continued for 24 hours until the peak attributed to isocyanate at 2270 cm^{-1} in the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy disappeared. The polymer solution was poured into a mould and dried at room temperature overnight to obtain the elastomers. LPU (Fig. 1(b) and Scheme S3, Fig. S4, Tables S2, S3, ESI†) and PUs crosslinked by trifunctional triethanolamine (TEA) (C(x)PU, where x refers to mol% of TEA units; Fig. 1(c) and Scheme S4, Table S4, ESI†) were obtained in a similar manner. In the ATR-FTIR spectra, the isocyanate absorption peak at 2270 cm^{-1} disappeared, and the absorption peaks at approximately 1683 cm^{-1} and 1722 cm^{-1} , attributed to the carbonyl groups, appeared after polymerization for all PUs (Fig. S5, ESI†).

The formation of movable crosslinking between TAc γ CD and the PU chain was confirmed by 2D nuclear Overhauser effect spectroscopy (NOESY) NMR spectroscopy. NMR spectroscopy of γ CDMe(13)PU was performed after sufficient swelling in chloroform- d (24 hours of swelling). Fig. 2 exhibits the NOE

correlation signals between the protons located on the internal side of the TAc γ CD rings (C(3)H 5.3 ppm) and the protons in the PU chain (a 1.5 ppm). In contrast, a NOE signal of C(3)H was not observed in the spectrum of the reference sample (Fig. S6, ESI†). These results suggest that the PU chains penetrated the TAc γ CD rings to form movable crosslinking.

2.2. Network structure of PU materials characterized by swelling tests

We performed swelling tests to study the amount of the movable crosslinking in the obtained PUs by immersing them in excess DCM (Fig. S7, ESI†). The swelling ratios were determined by the following equation.

$$\text{Swelling ratio} = \frac{W - W_0}{W_0} \times 100\%$$

where W is the weight of the swollen PU and W_0 is the initial weight of PU before the immersion. LPU with no crosslinking was dissolved, while γ CDMe(x)PU and C(x)PU were swollen. Moreover, the swelling ratio of γ CDMe(x)PU was larger than that of C(x)PU containing the same amount of crosslinking, which is a feature of movable crosslinking.⁵⁹ The swelling ratios of both chemical and movable crosslinking PU materials decreased with increasing contents of the TEA and TAc γ CD units, indicative of the formation of crosslinking by TEA and TAc γ CD. The DSC data obtained after eliminating the effect of processing history demonstrated that the glass transition temperature (T_g) increased upon the formation of crosslinking (Fig. S8, ESI†). The thermal decomposition temperatures of γ CDMe(x)PU and C(x)PU were higher than that of LPU, as determined by thermogravimetric analysis (TGA). The thermal decomposition temperatures of γ CDMe(x)PU and C(x)PU increased with the mol% of TAc γ CD and TEA units (Fig. S10, ESI†).

2.3. Mechanical properties of movable crosslinking PU

We investigated the mechanical properties of PUs by tensile tests. Fig. 3(a) and Fig. S11 in the ESI† show the stress-strain curves of γ CDMe(x)PU, C(x)PU, and LPU. γ CDMe(9)PU and γ CDMe(13)PU showed higher fracture stress (42 ± 4 MPa and 46 ± 3 MPa, respectively) than LPU (24 ± 2 MPa). The fracture stress of C(9)PU (42 ± 1 MPa) was close to that of γ CDMe(9)PU. When the amount of crosslinking units was increased to 13 mol%, the fracture stress of C(13)PU was increased to 44 ± 1 MPa. Fig. 3(b) shows the toughness and E values. The E values were determined from the slope at 0–5% strain of the curve. The E of γ CDMe(x)PU was enhanced with increasing the x mol% of TAc γ CD units. The E values of γ CDMe(9)PU (67 ± 1 MPa) and γ CDMe(13)PU (94 ± 1 MPa) were higher than that of LPU (57 ± 4 MPa), while the E values of C(9)PU (48 ± 2 MPa) and C(13)PU (50 ± 4 MPa) were lower than that of LPU. This result suggests that the formation of the movable crosslinking resulted in higher E values than the formation of covalent crosslinking.

The toughness was calculated from the integral of the stress-strain curve from the tensile test. C(9)PU and C(13)PU showed toughness values of 194 ± 5 MJ m^{-3} and 144 ± 4 MJ m^{-3} ,

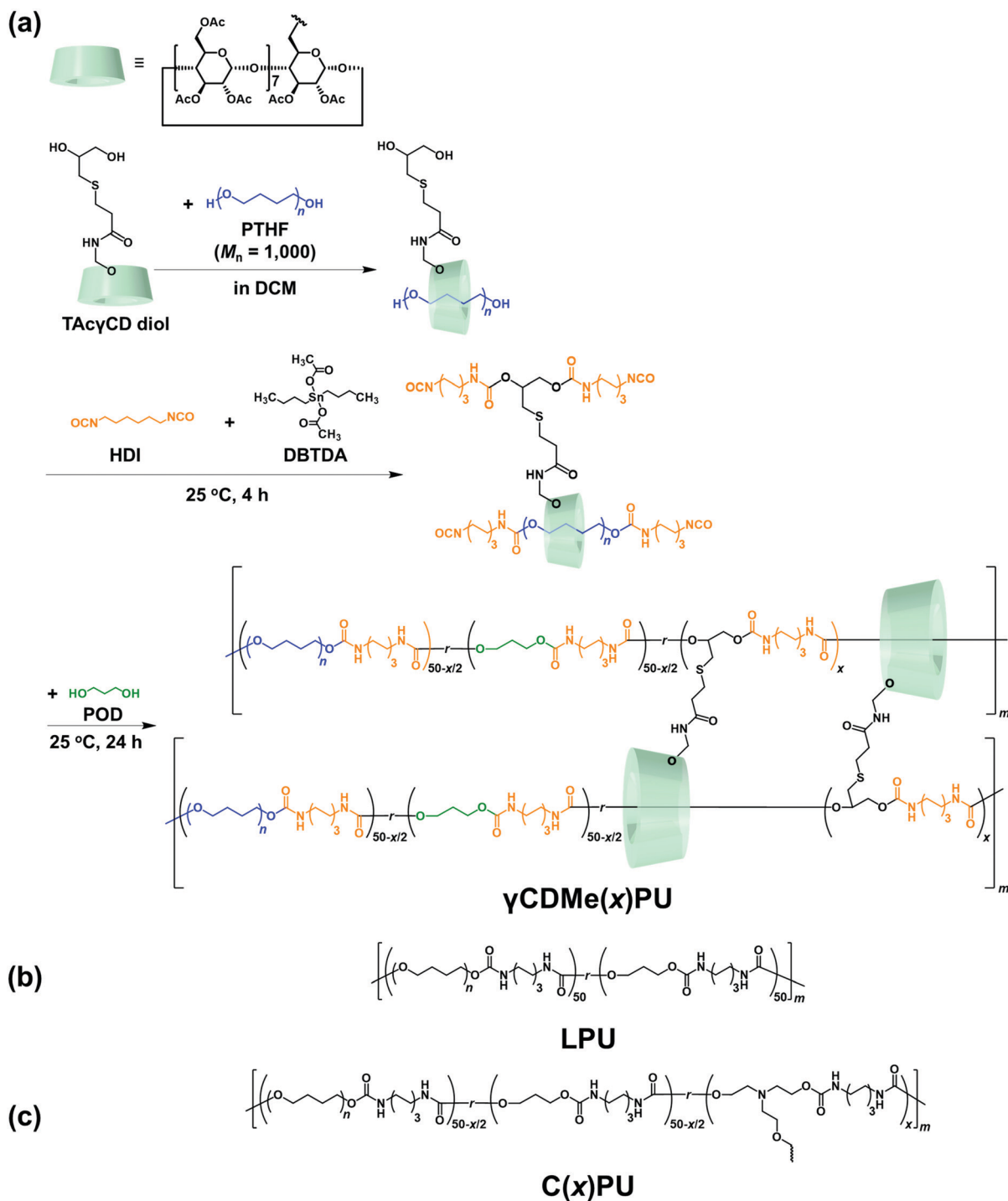


Fig. 1 (a) Synthesis of $\gamma\text{CDMe}(x)\text{PU}$ and chemical structures of (b) LPU and (c) C(x)PU, where x refers to the molar ratio of TAc γCD diol monomer or TEA monomer.

respectively, with a low E , while $\gamma\text{CDMe}(9)\text{PU}$ ($171 \pm 18 \text{ MJ m}^{-3}$) and $\gamma\text{CDMe}(13)\text{PU}$ ($146 \pm 19 \text{ MJ m}^{-3}$) showed higher toughness values than LPU ($145 \pm 14 \text{ MJ m}^{-3}$) with a high E . This result suggests that the introduction of TAc γCD into $\gamma\text{CDMe}(x)\text{PU}$ to form movable crosslinking played an important role in simultaneously improving the fracture stress, toughness, and E value.

Fig. 3(c) shows plots of toughness/ E versus E for $\gamma\text{CDMe}(x)\text{PU}$, C(x)PU, and LPU. The toughness/ E of C(x)PU decreased drastically with increasing E . On the other hand, the slope of the decrease in toughness/ E was moderate for $\gamma\text{CDMe}(x)\text{PU}$. The reason for these different changes depends on the nanostructure of the C(x)PU and $\gamma\text{CDMe}(x)\text{PU}$ materials. The nanostructure depends on the hydrogen bonding in the polyurethane materials and is an important

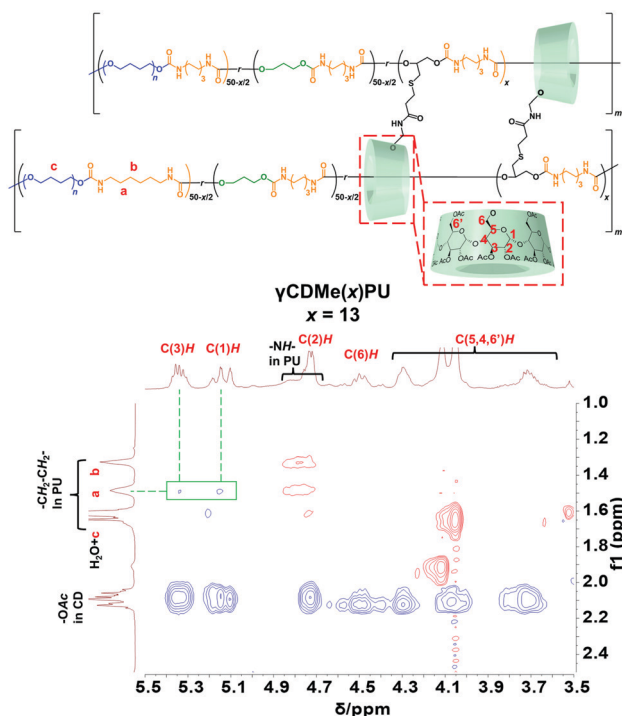


Fig. 2 600 MHz 2D NOESY NMR spectrum of γ CDMe(13)PU in chloroform-*d*. The NOE correlation signals between the TAC γ CD units and the PU main chains are highlighted.

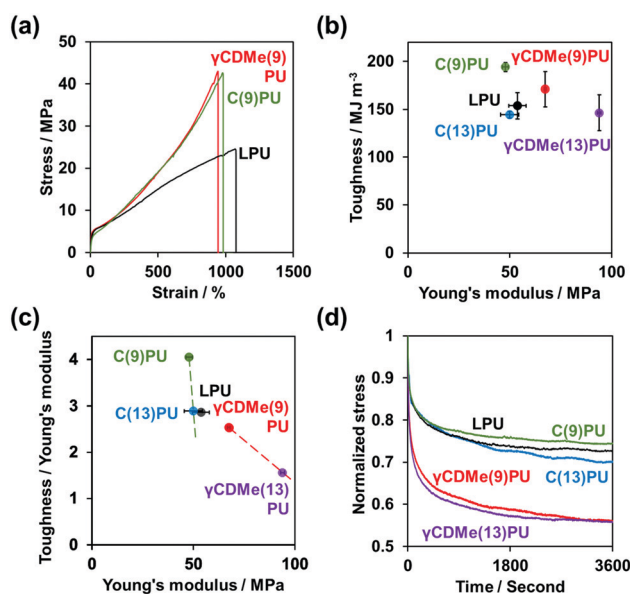


Fig. 3 (a) Stress-strain curves, (b) plots of toughness versus Young's modulus, (c) plots of toughness divided by Young's modulus and Young's modulus, and (d) relaxation time curves of LPU, γ CDMe(*x*)PU, and C(*x*)PU. The γ CDMe(*x*)PU showed higher fracture stress, Young's modulus, and shorter relaxation times than the LPU and C(*x*)PU.

factor affecting the Young's modulus. The introduction of chemical crosslinking may affect the formation of hydrogen bonds, resulting in no significant increase in the Young's modulus. We speculated that the effect would also occur with

the introduction of movable crosslinking, but the Young's modulus of γ CDMe(*x*)PU showed a significant increase. This indicated that the movable crosslinking improved the overall mechanical properties of the materials more than chemical crosslinking.

The relaxation time of PUs was investigated by stress relaxation tests (Fig. 3(d)). The γ CDMe(*x*)PU, C(*x*)PU, and LPU materials were stretched to 100% strain at a rate of 10 mm min^{−1}, and the strain was maintained for an hour. The stresses of the PU materials were normalized to focus on the behaviour of crosslinking. The results showed that γ CDMe(*x*)PU relaxed earlier than C(*x*)PU and LPU. To determine the relaxation time of the relaxable components and the ratio of relaxable components to the residual components of γ CDMe(*x*)PU, C(*x*)PU, and LPU, we carried out curve fitting using the Kohlrausch-Williams-Watts (KWW) models, as described by the following equation. All stress σ versus the stress relaxation time t curves of the samples were well fitted ($R^2 > 0.99$).

$$\sigma = \sigma_r \exp \left\{ - \left(\frac{t}{\tau} \right)^\beta \right\} + \sigma_\infty$$

where σ_r (relaxable stress), σ_∞ (residual stress), τ (relaxation time), and β (stretching exponent) are fitting parameters. Table 1 summarizes the obtained fitting parameters. The τ of γ CDMe(9)PU and γ CDMe(13)PU indicated fast relaxation (small values of τ) and lower residual stresses. Although the τ values of C(9)PU and LPU were also short, the residual stresses were higher. With the increase in *x* mol%, τ of C(13)PU increased, and the final residual stress was lower. γ CDMe(*x*)PU achieved both rapid relaxation and effective reduction of residual stress.

The hysteresis of the PU materials was also investigated by cyclic stretching tests. γ CDMe(*x*)PU, C(*x*)PU, and LPU were stretched to 50% strain and then returned to 0% strain 5 times. Fig. 4(a–c) and Fig. S12 in the ESI† show the results of the cyclic tensile tests. Based on the area of the stress-strain curves during stretching and recovery, we calculated the hysteresis loss (Fig. 4(d)). C(9)PU, C(13)PU, and LPU produced almost the same hysteresis loss in the first cycle. In contrast, the hysteresis loss of γ CDMe(*x*)PU increased with increasing *x* mol%. This result suggests that the movable crosslinking of γ CDMe(*x*)PU effectively dissipates energy and prevents stress concentration when the chains undergo large rearrangements in the first cycle. In the second cycle, the hysteresis losses of C(9)PU, C(13)PU, and LPU decreased rapidly, and after five cycles, the

Table 1 Relaxable and residual components of the PU materials were determined using the KWW models

PU materials	Relaxable components			Residual components
	σ_r^a/σ_0^e	τ^b/s	β^c	$\sigma_\infty^d/\sigma_0^e$
γ CDMe(9)PU	0.52	96	0.27	0.48
γ CDMe(13)PU	0.50	59	0.31	0.50
C(9)PU	0.30	86	0.29	0.70
C(13)PU	0.42	1047	0.26	0.58
LPU	0.29	148	0.35	0.71

^a Relaxable stress. ^b Relaxation time. ^c Stretching exponent. ^d Residual stress. ^e Initial stress.

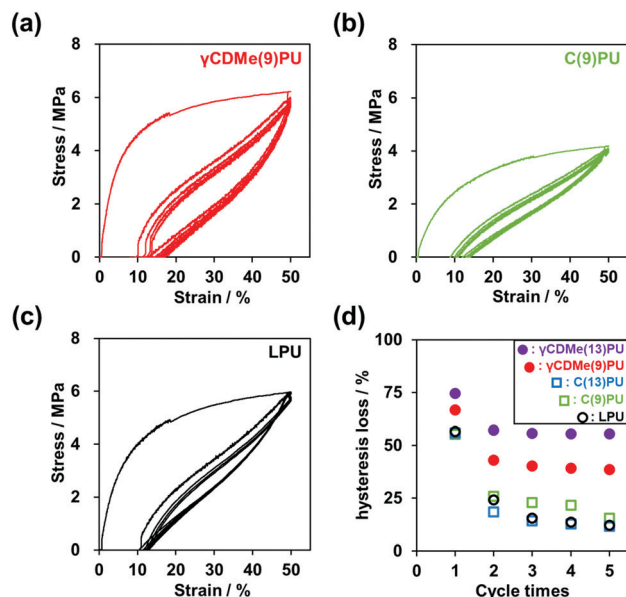


Fig. 4 The cyclic stress–strain curve with fixed strain (50%) of (a) γ CDMe(9)PU, (b) C(9)PU and (c) LPU. (d) Hysteresis loss calculated from the cyclic stress–strain curve. The cycles were performed five times.

hysteresis losses were low. However, the hysteresis losses of both γ CDMe(9)PU and γ CDMe(13)PU remained constant from the second cycle, and the hysteresis loss of γ CDMe(13)PU was higher than that of γ CDMe(9)PU after 5 cycles. γ CDMe(x)PU maintains a higher hysteresis loss than C(x)PU and LPU due to the presence of movable crosslinking.

Furthermore, according to the DSC data of the PU materials before and after the cyclic stretching tests (Fig. S9, ESI[†]), the melting points (T_m) of C(9)PU, C(13)PU, and LPU increased slightly, and in contrast, the T_m of γ CDMe(9)PU and γ CDMe(13)PU decreased. The crystals of C(9)PU, C(13)PU, and LPU required much thermal energies after stretching, while the crystals of γ CDMe(9)PU and γ CDMe(13)PU required less. After stretching, the T_g of γ CDMe(9)PU, γ CDMe(13)PU, and LPU decreased. γ CDMe(9)PU, γ CDMe(13)PU, and LPU tended to soften after cyclic stretching. These results indicate that the hysteresis, T_m , and T_g of γ CDMe(x)PU are different from those of C(x)PU and LPU.

2.4. Stretching effect of hydrogen bonds in γ CDMe(9)PU observed by *in situ* FT-IR testing

We performed *in situ* FT-IR spectroscopy with tensile testing, as shown in Fig. 5. Fig. 5(a, c and e) show the stretching mode of the carbonyl (C=O) group (black line) of C(9)PU, LPU, and γ CDMe(9)PU before tensile stretching. After baseline calibration and normalization (based on the hydrocarbon band at 2856 cm^{-1}), the bands of C(9)PU, LPU, and γ CDMe(9)PU (black line) were separated into three, three, and five bands, respectively (red lines in Fig. 5(a, c and e)).

The long diol chain segment (here, PTHF) is usually called the “soft segment”. The short diol chain with the isocyanate (here is POD + HDI) is called the “hard segment”.⁵⁷ Therefore, the C=O groups localized in the hard segments.⁵⁸

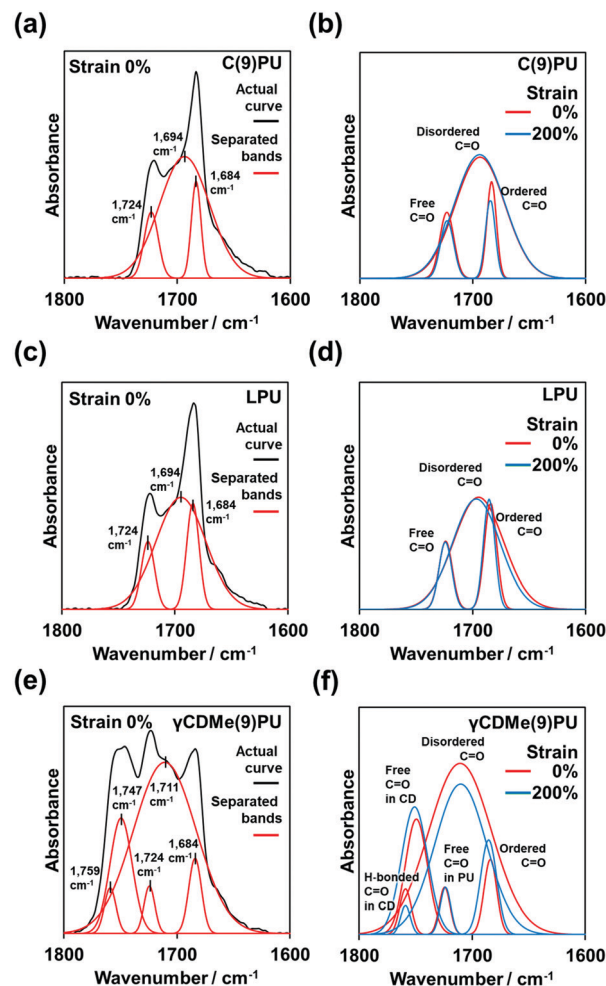


Fig. 5 Actual FT-IR spectra and separated bands after peak deconvolution of C(9)PU (a), LPU (c), and γ CDMe(9)PU (e) before tensile stretching. Changes in the separated bands of C(9)PU (b), LPU (d), and γ CDMe(9)PU (f) during tensile stretching from 0% to 200% strain.

Fig. 5 shows the ordered C=O groups band in the ordered hard segments at 1684 cm^{-1} and the disordered C=O groups band in the disordered hard segments at 1694 cm^{-1} . The bands at 1684 cm^{-1} and 1694 cm^{-1} were assigned to the C=O groups with hydrogen bonds between the hard–hard segments. The band at 1724 cm^{-1} was assigned to the C=O groups without hydrogen bonds.⁵⁹ Fig. 5(b) shows the changes in the relevant bands upon stretching the C(9)PU specimen from 0% to 200% strain. The band intensity of the ordered C=O groups decreased after stretching, and the band intensity of C=O groups without hydrogen bonds also decreased after stretching, but the band intensity of the disordered C=O groups almost no changes (or increased slightly). We postulated too large area of the disordered C=O groups band caused the no (or small) change to observe. Namely, the ordered hard segments would dissociate into disordered segments after tensile stretching. The total number of hydrogen bonds in the stretched C(9)PU increased.

The positions of the bands in the LPU spectrum are similar to those in the C(9)PU spectrum. The band intensity of the

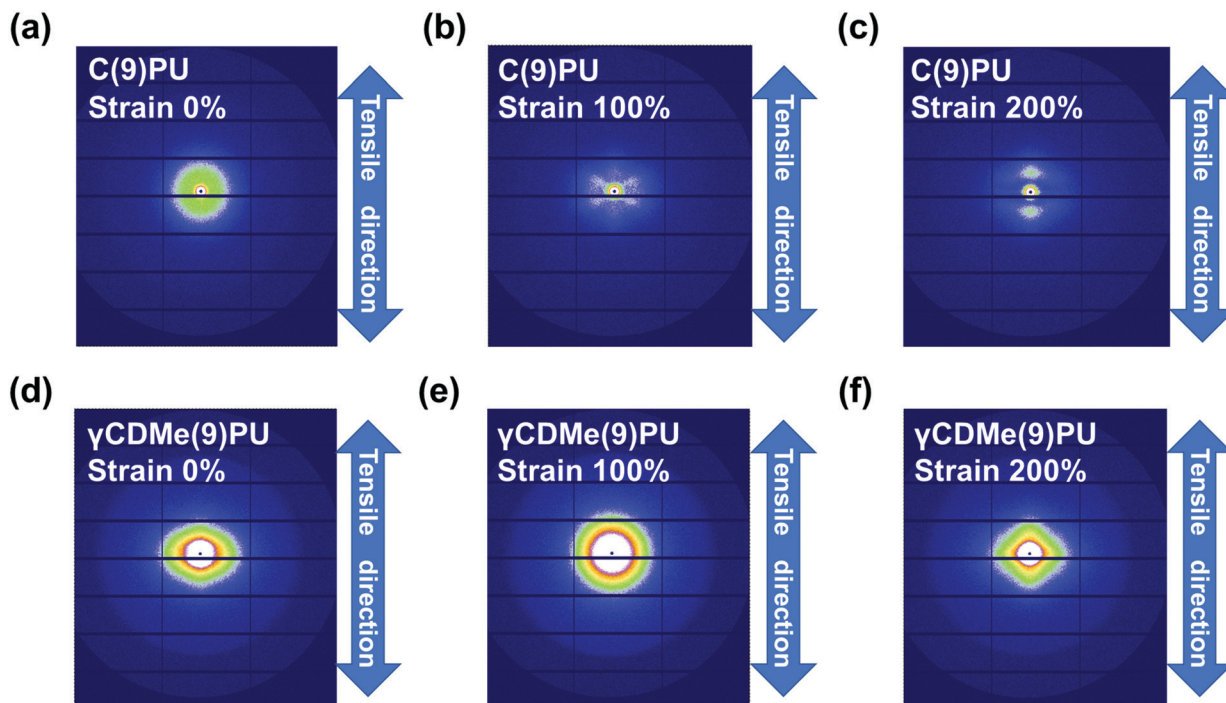


Fig. 6 2D small-angle X-ray scattering (SAXS) patterns of (a–c) C(9)PU and (d–f) γ CDMe(9)PU with 0%, 100% and 200% strain. The direction of tensile testing is shown by the arrow.

change in the 2D SAXS patterns was observed during stretching (Fig. 6(d–f)). The 2D SAXS patterns of LPU were similar to those of C(9)PU. The scattered light intensity of LPU in the tensile direction diminished upon stretching to 100% strain but enhanced upon stretching to 200% strain due to the shish-kebab orientation (Fig. S13(a–c), ESI†).

The SAXS profiles of C(9)PU showed peaks caused by microphase separation in the tensile direction and vertical direction at 0% strain (Fig. 7(a and b)). When C(9)PU was stretched to 100% strain, the intensities of the peaks in both directions decreased. When the samples were stretched to 200% strain, the intensity of the peak in the vertical direction continued to decrease, while that of the peak in the tensile direction increased again. This result proves that the shish-kebab orientation is formed in the tensile direction of C(9)PU and increases the degree of microphase separation. The microphase separation caused by the shish-kebab orientation can increase the stress of C(9)PU; however, we speculate that when the action of this orientation is too strong, the toughness of the material decreases, leading to the steep slope observed in Fig. 3(c).

The SAXS profiles of LPU were also similar to those of C(9)PU. The scattered light intensity of LPU diminished when the sample was stretched to 100% strain but enhanced due to shish-kebab orientation along the tensile direction when the sample was stretched to 200% strain (Fig. S13(d and e), ESI†).

The SAXS profiles of γ CDMe(9)PU also showed peaks in the tensile direction and vertical direction at 0% strain (Fig. 7(c and d)). When the strain increased, the intensities of peaks in both directions decreased and no peak was generated in the tensile direction, similar to that of C(9)PU, at 200% strain. This result

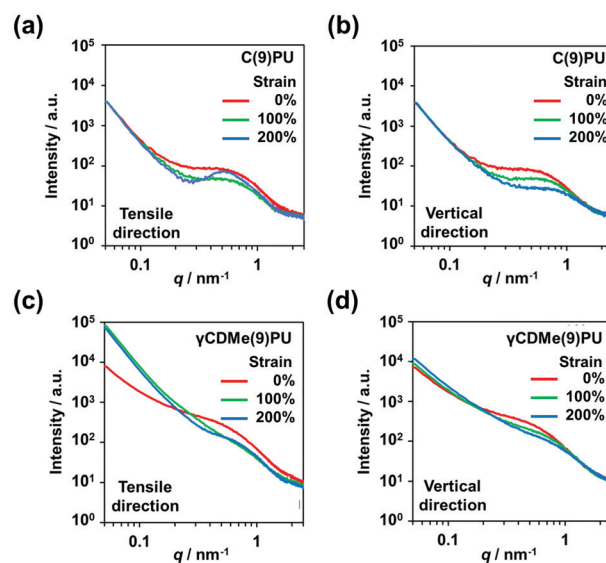


Fig. 7 SAXS profiles of C(9)PU with 0%, 100% and 200% strains in the (a) tensile and (b) vertical directions. SAXS profiles of γ CDMe(9)PU with 0%, 100% and 200% strains in the (c) tensile and (d) vertical directions.

indicates that the introduction of movable crosslinking hinders the shish-kebab orientation during stretching and is an important reason for its mechanical properties to maintain high toughness at a high Young's modulus. In addition, the scattered light intensity of γ CDMe(9)PU was significantly enhanced upon stretching the sample from 0% to 100% in the tensile direction when the scattering vector (q) < approximately

0.2 nm⁻¹ (Fig. 7(c)). This result indicates that the movable crosslinking units were pulled in γ CDMe(9)PU.

The formation of the shish-kebab orientation can also account for the change in hydrogen bonding described in the previous section. The aggregation of hard segments due to orientation promotes the enhanced hydrogen bonding of C(9)PU during stretching. In contrast, the movable crosslinking suppressed the formation of this orientation. γ CDMe(9)PU showed a decrease in hydrogen bonding during stretching.

In situ WAXS measurements with stretching were used to investigate the changes in the crystallinity of C(9)PU, γ CDMe(9)PU, and LPU. The scattered light intensity of C(9)PU, γ CDMe(9)PU, and LPU decreased with stretching, and these decreases were slow in the vertical direction, as shown in the 2D WAXS patterns (Fig. S14, ESI†). The new shoulder peaks appeared with stretching at approximately $q = 17 \text{ nm}^{-1}$ in the vertical direction of the WAXS profiles of C(9)PU and LPU (Fig. S15(a and c), ESI†). New shoulder peaks were not observed in the WAXS profiles of γ CDMe(9)PU (Fig. S15(e), ESI†). In the tensile direction, the peak intensities of C(9)PU, γ CDMe(9)PU, and LPU were decreased (Fig. S15(b, d, and f), ESI†).

These results indicate that the crystallinity of C(9)PU and LPU that stems from the shish-kebab orientation along the tensile direction increases with stretching. No relevant changes were observed in γ CDMe(9)PU, which indicates that the presence of movable crosslinking makes the polyurethane chain less susceptible to shish-kebab orientation.

3. Conclusions

Here, a PU elastomer with movable crosslinking was successfully prepared *via* the introduction of TAC γ CD and was named γ CDMe(x)PU. γ CDMe(x)PU showed similar fracture stresses and strains to C(x)PU with the same number of crosslinking units but higher *E* values, as determined by the tensile tests. The results of the cyclic tensile tests showed that the movable crosslinking of γ CDMe(x)PU effectively dissipated energy and prevented stress concentration. The tensile tests of the relaxation time demonstrated that γ CDMe(x)PU achieved both rapid relaxation and effective reduction of residual stress. Hydrogen bonds formed between the C=O groups of the TAC γ CD units and the hard segments in γ CDMe(x)PU, according to the *in situ* FT-IR measurements. The synergistic effect of the movable crosslinking and the hydrogen bonds in γ CDMe(x)PU contributed to the simultaneous increase in the mechanical properties such as Young's modulus and toughness. Moreover, the two components suppressed the shish-kebab orientation along the tensile direction, according to the *in situ* SAXS and WAXS measurements. We believe that this work will provide a design guidance for the fabrication of new tough polymer elastomers. γ CDMe(x)PU with both high toughness and high Young's modulus are expected to become more important and be used in practical applications in the future.

Author contributions

C. J. performed the syntheses and spectroscopic studies. All authors contributed to the characterizations and discussion. Y. I. discussed and explained the results of the FT-IR spectroscopy. G. M. discussed and explained the results of the SAXS and WAXS measurements. C. J., J. P., and Y. T. co-wrote the paper. M. O., A. H., and H. Y. provided valuable suggestions. H. S., H. T., and Y. O. supported the syntheses of the monomer. Y. T. conceived and directed the study. Y. T. oversaw the project and contributed to the execution of the experiments and interpretation of the results.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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