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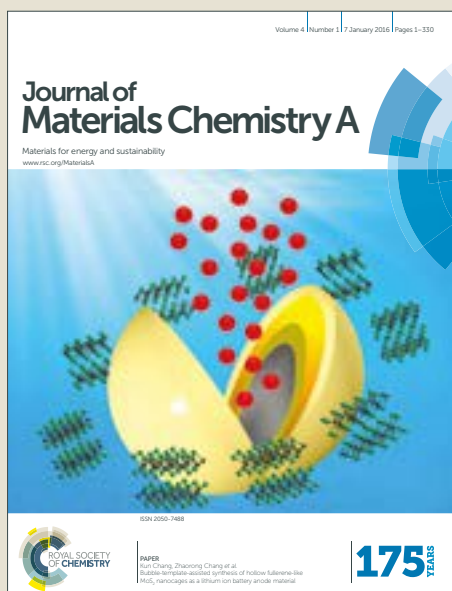


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Facile Synthesis of Novel Elastomers with Tunable Dynamics for Toughness, Self-healing and Adhesion

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Key words

elastomers, tough and self-healing, adhesion, relaxation time, linear rheology

Abstract

In this work, we develop a series of novel elastomers from acrylate monomers by one-step free radical copolymerization without using organic solvents. The dynamics of the elastomers, characterized by the Kuhn segment relaxation time τ_0 , is tuned over six orders by varying the structure and composition of the acrylate monomers. Comprehensive studies on the linear rheology at small deformation and tensile/fracture behaviors at large deformation of the materials are performed. A universal ductile-brittle transition of the elastomers around the

criterion of $\dot{\epsilon} \cdot \tau_0 \approx 0.1$ is observed for the diverse monomer pairs and stretch strain rate $\dot{\epsilon}$ and the elastomers exhibit maximum energy dissipation around the ductile-brittle transition reaching a work of extension at fracture of $\sim 25 \text{ MJ/m}^3$ and a fracture energy of 20 kJ/m^2 . Such toughness is comparable to natural rubbers and is among the highest ever reported. In addition, these elastomers possess 100% self-recovery, and a relatively high self-healing efficiency (37%-70%) of cutting samples at room temperature even for relatively rigid samples and strong adhesive strength on glass and polymethylmethacrylate (PMMA) substrates. The universal ductile-brittle transition of the materials means that we can use the linear rheology dynamics as fingerprints for predicting dynamic spectra of toughness of the materials. The wide range of tunable dynamics substantially enriches the choices of elastomers for various applications, and the facile and solvent-free synthesis of these elastomers are eco-friendly, cost-effective and scalable, which greatly lowers the barrier for the practical applications.

1. Introduction

Elastomers, known for their softness and stretchable ability are extensively used as structural materials where load-dispersing and shock-absorbing abilities are required, such as in automotive accessories, foot wear and bridge bearings.^[1] Although natural rubbers have demonstrated excellent mechanical performance, many synthetic substitutes have been developed due to the inherent limitations of natural resources. A current limitation of synthetic elastomers is that they are often stretchable but lack toughness, breaking easily along a notch, as seen in polydimethylsiloxane (PDMS) elastomer, for example.^[2] Poor mechanical toughness often results in catastrophic failure of the materials, especially during long-term usage, which directly impacts safety and service life time.^[3] To enhance the toughness of a material, it is necessary to increase the energy dissipation against the crack propagation. The state-of-the-art approaches to enhance mechanical energy dissipation include incorporating of crystalline or glassy domains and nano-fillers to the matrix,^[4-6] inducing of covalent sacrificial bonds by multiple network structures based on the double

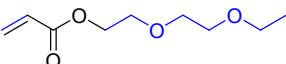
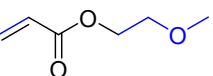
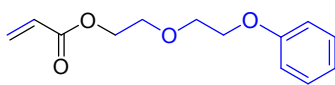
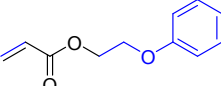
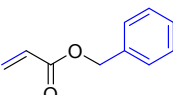
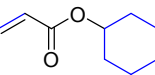
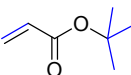
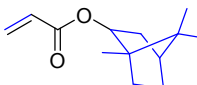
network concept,^[7-10] and of reversible sacrificial bonds by ionic interactions, hydrogen bonds, etc.^[11-25] These approaches, however, usually need complicated synthesis processes, which limits their applicability for wide use where simple processing, cost effective, eco-friendly, scalability are required. In this work, we intend to develop a series of tough, self-healing and adhesive elastomers with tunable mechanical properties by simple one-step synthesis without using solvents.

Previous studies have shown that viscoelastic energy dissipation results in the toughness of polymeric materials, and the crack propagation resistance can be related to the linear viscoelastic behaviors of the polymers.^[26-30] Here, we apply this general understanding on the relationship between linear rheology and mechanical properties to guide the molecular design and development of new tough and high strength elastomers. It is well-established that materials constructed from highly entangled linear polymers have a wide dynamic mechanical spectrum, featuring several relaxation times: the shortest relaxation time, τ_0 , related to the Kuhn segment motion; the relaxation time, τ_e , related to the Rouse motion of entangled strands with N_e Kuhn segment, $\tau_e = \tau_0 N_e^2$; and the reptation time, $\tau_{Rep} = 6\tau_0 N^3/N_e$, the time required for the whole chain with N Kuhn segments to escape from its tube.^[31] The mechanical behavior of polymeric materials depends on the relationship between the observation time scale, t , that is the inverse of deformation strain rate, $\dot{\epsilon}$, and these relaxation times. For $t \ll \tau_0$, the Kuhn segment cannot relax during deformation and the material exhibits glassy behavior with a shear storage modulus, $G_g \approx G_{(\tau_0)} \approx kT/v_0$, where v_0 is the volume of the Kuhn segment. When $\tau_0 < t < \tau_e$, the Rouse motion of entangled strands are seen, and the material is viscoelastic, showing a frequency dependence of the storage modulus $G' \sim \omega^{0.5}$. When $\tau_e < t < \tau_{Rep}$, the Rouse motion of entangled strands are relaxed, and the materials are in rubbery state, showing a plateau storage modulus, $G_e = G_{(\tau_e)} = kT/v_0 N_e$. Here, kT is the thermal energy. For $t > \tau_{Rep}$, the material exhibits liquid-like flow. For a material with an extremely long τ_{Rep} compared to the real application time window, the material behaves as a polymeric solid with viscoelastic properties around $\tau_0 < t < \tau_e$.

To apply the above well-established rheological knowledge for the facile material development, we choose a series of commercially acrylate monomers. These monomers are in liquid form at room temperature and their homopolymers have a wide range of glass transition temperature, corresponding to significantly different Kuhn segment motions varying over six orders in relaxation time. We perform the free radical copolymerization of liquid binary mixtures of acrylate monomers without using any organic solvents. By tuning the composition, we obtain amorphous copolymers with Kuhn segment relaxation times, τ_0 , at any desired values between those of the two components. Based on this strategy, we synthesized several series of copolymers from various pairs of acrylate monomers, with τ_0 tunable over six orders of magnitude. We comprehensively studied the rheological behaviors of the polymers, and found that universally the toughness of these copolymers at large deformation increase with the deformation strain rate, $\dot{\epsilon}$, and reach maximum values at a critical condition $\dot{\epsilon} \cdot \tau_0 \approx 0.1$. Beyond this critical value, the materials become brittle. The maximum fracture energy is as high as 20 kJ/m², comparable to that of natural rubber and recently developed tough elastomers.^[10,12-25,32-34] Furthermore, the short Kuhn segment relaxation times give rise to high mobility of polymer chains, affording the materials to heal the fractured surfaces after cutting and adhere on the different substrates at room temperature. Therefore, the elastomers show the high self-healing ability with a high healing efficiency as high as 47.6% even the sample with a high elastic modulus (≈ 27 MPa). And the elastomer adheres to the glass substrate showing a critical energy release rate of ~ 280 J/m² by the lap-shear test. This investigation reveals that the most tough soft materials at large deformation can be predicted from the linear rheological behavior obtained at small deformation. We believe such a comprehensive study on the dynamics of synthetic copolymers provides a guide to design tough elastomers.

2. Results and Discussion

Scheme 1. Chemical structures of acrylate monomers used in this work. The glass transition temperature, T_g , of the corresponding homopolymer is also shown. The order is arranged according to glass transition temperature.

Monomer	Structure	T_g of homopolymer (°C)
DEEA		-57
MEA		-34
PDEA		-12
PEA		10
BZA		11
CHA		33
TBA		49
IBA		74

Scheme 1 shows the chemical structures of the acrylate monomers used in this work. They are shown in two groups, according to whether the T_g of the homopolymer is above or below room temperature (**Figure S1**). All monomers are liquid at room temperature and are miscible in all compositions. Using an ultraviolet initiator, benzophenone, that is soluble in the liquid monomers, copolymerization was performed without the use of any solvents. To tune the relaxation times of the copolymers over a wide range by varying the monomer composition, we chose pairs of acrylate monomers whose homopolymers possess very

different glass transition temperatures: compared to the observation temperature (24 °C), one monomer with a lower T_g and the other with a higher T_g were selected. We expect that the significant difference in T_g relates to very different Kuhn segment relaxation times, τ_0 . Low T_g polymers have fast relaxation times, and *vice versa*. The samples are coded as P(A-*co*-B) (F), where A and B are the abbreviations of monomers with T_g of their homopolymers lower and higher than the room temperature, respectively, and $F = [B]/([A]+[B])$ indicates the molar fraction of B monomer in the copolymer.

First, as a typical example, we studied the copolymer P(PEA-*co*-IBA), formed from ethylene glycol phenyl ether acrylate (PEA) and isobornyl acrylate (IBA). The T_g of their corresponding homopolymers, PPEA and PIBA, are 10 °C and 74 °C, respectively. We obtained optically transparent (**Figure 1**) and amorphous copolymers without phase separation for various molar fractions of IBA, F , as confirmed by Small-Angle X-ray Scattering (SAXS) and Wide-angle X-ray Scattering (WAXS) (**Figure S2**), suggesting that PEA and IBA are randomly distributed along the copolymer chains.

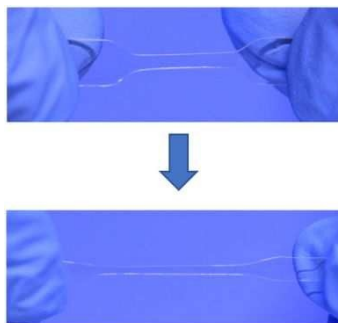


Figure 1. Appearance of elastomers before and at stretching. All elastomers are highly transparent.

We studied the linear rheological behavior of the copolymers via a rheometer. Based on the principle of time-temperature superposition, we were able to construct the dynamic mechanical spectrum over 14 orders in frequency $a_T \cdot \omega$ by performing oscillatory shear frequency ω sweeps from 0.1 to 100 rad/s at a small shear strain of 0.1% over a wide temperature range. **Figure 2a - c** show exemplary master curves of the dynamic shear modulus, for PPEA ($F = 0$), P(PEA-*co*-IBA) ($F = 0.4$), and PIBA ($F = 1$). Results of copolymers with other compositions, F , are shown in **Figure S3**. The temperature

dependence of the horizontal shift factors, a_T , used to construct the master curves are shown in **Figure S4**. In the wide angular frequency window, we see that all of the copolymers, like the homopolymers of PPEA ($F = 0$) and PIBA ($F = 1$), show dynamic spectrums characteristic of amorphous polymers with a well-defined rubbery-glassy transition. The rubbery-glassy transition shifts to lower angular frequencies with increasing F by several orders of magnitude, while the plateau storage modulus, G' , in the rubbery region ($10^4 \sim 10^5$ Pa) and glassy region ($10^7 \sim 10^8$ Pa) only weakly varied with F . In the transition region, the dynamic shear modulus, both the storage modulus, G' , and the loss modulus, G'' , increased with frequency, ω , as a power-law relation, close to the Rouse mode motion, $G', G'' \sim \omega^{0.5}$.^[35] The above results show that for the copolymers, F only influences the effective frictional dynamics of the monomer, while the polymer chains maintain similar dynamic features. In addition, the horizontal shift factor, a_T , roughly shows a simple Arrhenius dependence with temperature, which is characteristic of dynamics that originate from friction (**Figure S4**).^[36] From these dynamic mechanical spectra, we conclude that the polymers obtained are amorphous, without specific associations between polymers, although the polymer dynamics can be varied over many orders in frequency by tuning F . Accordingly, we correlated the dynamic rheological parameters with the molecular structure using the theory for flexible linear polymer melts, and the results are summarized in **Table S1**. The relaxation time of the Kuhn segment motion, τ_0 , was obtained by the inverse of angular frequency where the loss modulus, G'' , reaches a peak in the dynamic mechanical spectrum and crosses over the storage modulus G' .^[28] The homopolymer PPEA has a very short $\tau_0 \sim 4.0 \times 10^{-4}$ s, indicating that the monomer PEA possessing a phenyl side group with a relatively long spacer is very mobile (**Figure 2a**). On the other hand, the homopolymer PIBA has a very long $\tau_0 \sim 3.8 \times 10^2$ s, indicating that the bulky isobornyl group substantially hinders the motion of the IBA segment (**Figure 2c**). We notice that PIBA shows a much broader rubbery-glassy transition but slightly lower glassy modulus, G_g , than those of PPEA. The latter can be understood by the relatively bulky isobornyl group of IBA, which leads to a larger Kuhn segment volume, v_0 , than that of the PEA, since $G_g = kT/v_0$, where k is the Boltzmann constant, and T is the

temperature. The relaxation time of the Kuhn segment, τ_0 , is related to the effective viscosity, ζ , and Kuhn length, b , of the monomer by $\tau_0 = \zeta b^2 / 6\pi^2 kT$.^[31] Since b should not change significantly for different monomers, we see that the effective viscosity of the PIBA, with bulky isobornyl groups, is larger by several orders of magnitude than those of the PPEA with phenyl groups. The copolymers exhibited a well-defined, single relaxation time, τ_0 , that falls in between that of the two homopolymers (**Figure 2b**, **Figure S3**). τ_0 monotonously increases with increasing molar fraction F of IBA in the logarithmic plot, and then saturates at $F = 0.7$, as shown in **Figure 2d**. The saturated τ_0 suggests that the dynamics of the copolymer is dominated by IBA at large F .

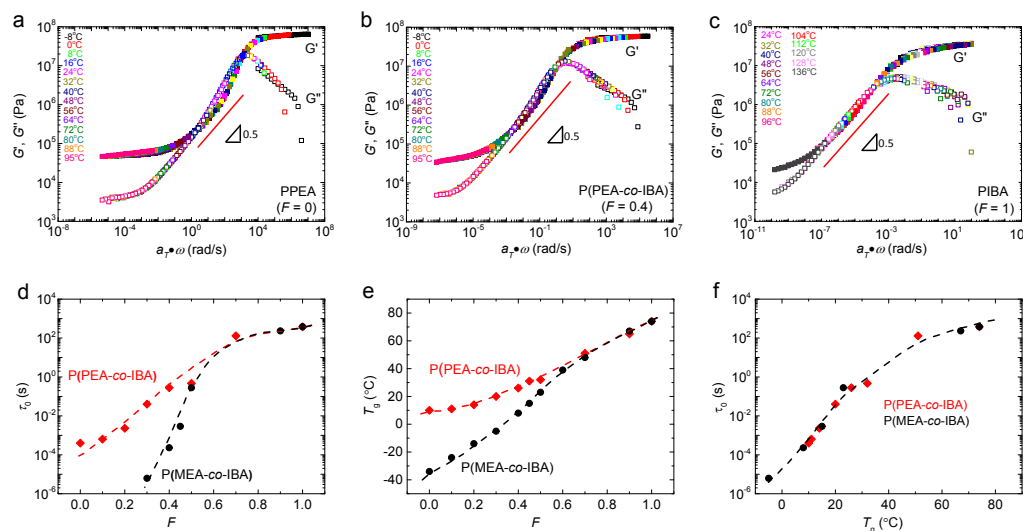


Figure 2. Typical master curves of G' and G'' of P(PEA-co-IBA) elastomers at different IBA fractions, F , at 24 °C. (a) $F = 0$ (PPEA); (b) $F = 0.4$; (c) $F = 1$ (PIBA). (d-f) Dynamic and thermal properties of P(PEA-co-IBA) and P(MEA-co-IBA) elastomers at various F . (d) Logarithmic plot of Kuhn segment relaxation time τ_0 and F at 24 °C. (e) Linear plot of glass transition temperature T_g and F . (f) Logarithmic plot of τ_0 and T_g . The Kuhn segment relaxation time, τ_0 , of P(MEA-co-IBA) ($F < 0.3$) is too short to be observed. The solid lines in (a) - (c) have a slope of 0.5. The dotted lines in d-f are guides for the eye.

The relaxation time related to the Rouse motion of entangled strands, τ_e , was obtained from the inverse of the angular frequency when crossover of the storage modulus G' and loss modulus G'' occurs (**Table S1**).^[31] We see that τ_e is approximately $10^3 \sim 10^4$ times greater

than τ_0 , and increases with F . From $\tau_e = \tau_0 N_e^2$, the number of Kuhn segments between entanglement, N_e , is about 30 ~ 100, and independent of F . This result again confirms that there are no inter-chain polymer associations. It should be mentioned that for associating polymers, the modulus ratio, G_g/G_e , between the glassy state and the rubbery state is proportional to the stick number N_s between the entangled strands, which should increase with F if the high T_g component IBA forms associations.^[37] For all copolymers, no polymer flow is observed and the reptation times, τ_{Rep} , are beyond the longest observation times (in a time window 10^6 s ~ 10^{10} s as estimated from $F = 0$ and $F = 1$). This result indicates that the polymers behave like solids up to an observation time of at least 12 - 120000 days depending on F at 24 °C. In the observation time window of $\tau_0 < t < \tau_e$, the materials are viscoelastic solids.

The copolymers show a single glass transition temperature, T_g , that falls in between the T_g of the two homopolymers, as confirmed by differential scanning calorimetry (DSC) (**Figure S1**). With increasing IBA content, T_g of the resulting polymers increased (**Figure 2e**). This is in consistent with previous reports on acrylate polymers.^[38, 39] Here we see a logarithmic correlation between τ_0 and T_g , except for large F , as shown in **Figure 2f**. These results show that the change in glass transition temperature within a range of -5 °C ~ 50 °C brings about a change in the characteristic relaxation times over a range as wide as 10^{-5} s ~ 10^3 s.

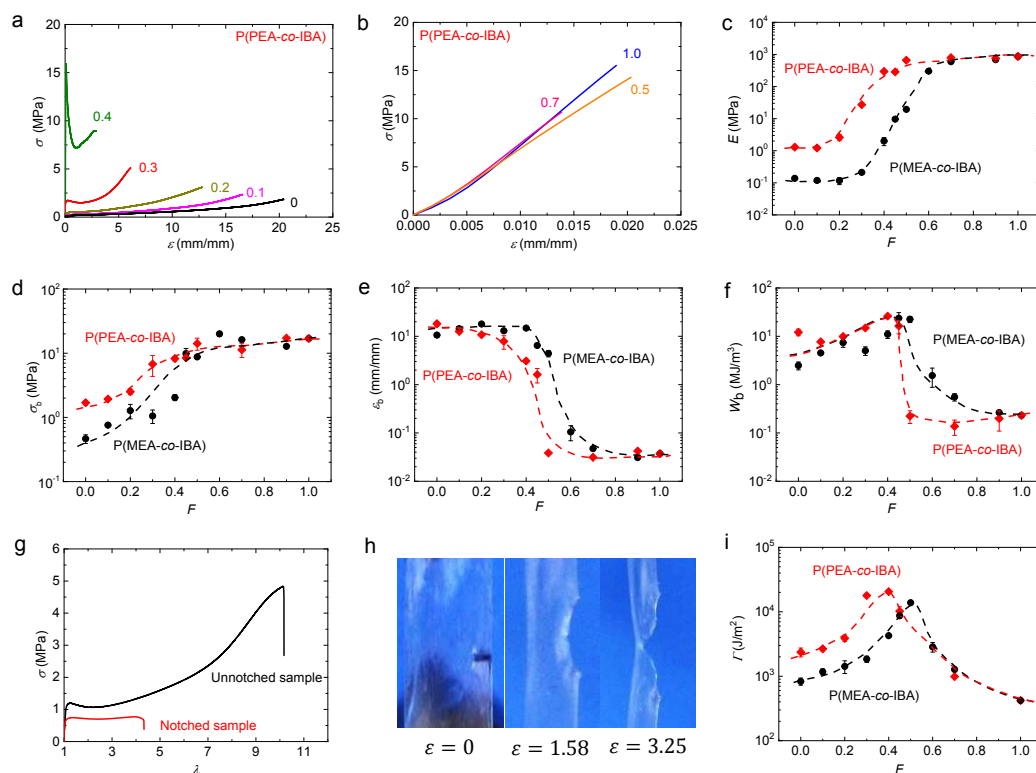


Figure 3. Mechanical properties of P(PEA-*co*-IBA) and P(MEA-*co*-IBA) elastomers with varied IBA molar fraction, F , at a strain rate 0.14 s^{-1} , at room temperature (24°C). (a, b) Stress-strain curves of P(PEA-*co*-IBA) elastomers with F from 0 to 0.4 (a), and above 0.5 (b). F dependence of Young's modulus E (c); fracture stress σ_b (d); fracture strain ϵ_b (e); and work of extension to fracture W_b (f). The numbers in (a) and (b) are F of the copolymers. (g) Typical stress versus stretch curves for un-notched and notched samples of P(PEA-*co*-IBA) ($F = 0.3$) at a strain rate of 0.083 s^{-1} ; (h) Photo images of crack propagation process for notched sample of P(PEA-*co*-IBA) ($F = 0.3$) at stretching; (i) Fracture energy Γ of P(PEA-*co*-IBA) and P(MEA-*co*-IBA) elastomers at various F measured by single-edge notch test at a strain rate of 0.083 s^{-1} . Each data point represents the average of three measurements. The dotted lines in c-f and i are guides for the eye.

Next, we study how does the linear dynamics of the polymers at small deformation influence the mechanical behavior at large deformation and fracture. We studied the tensile behaviors of samples with varied F at the same initial strain rate. **Figure 3a** and **3b** shows typical tensile stress-strain curves of P(PEA-*co*-IBA) with various F at a strain rate of 0.14 s^{-1} . For F from 0 - 0.4 (**Figure 3a**), the elastomers, having T_g below ambient temperature, are very ductile

with a clear yield point at small deformation which substantially enhances the toughness of the sample. When F is increased from 0.5 to 1 (**Figure 3b**), the T_g increases to above ambient temperature, and the material become rigid and brittle with a very low fracture strain. The mechanical properties including Young's modulus, E , fracture stress, σ_b , fracture strain, ε_b , and work of extension, W_b , with varied F are summarized in **Figure 3c-3f**. Increases in E (1 - 800 MPa) and σ_b (1.7 - 17.0 MPa) and decrease in ε_b (20 - 0.04 mm/mm) with increasing F was observed (**Figure 3c, 3d, 3e**). The work of extension, W_b , the area below the stress-strain curve that describes the mechanical toughness of elastomers, increased with F initially, reaching a maximum value ($\approx 25 \text{ MJ/m}^3$) around $F = 0.4$, and then drops rapidly (**Figure 3f**). This value is much higher than the reported acrylate polymer system ($\sim 1 \text{ MJ/m}^3$) and it is very impressive for amorphous polymers.^[40] We consider that the much higher toughness in the present system is mainly a result of their viscoelastic features, providing the large bulk energy dissipation during the deformation.

To evaluate the fracture toughness of the materials, the fracture energy was measured by the single-edge notch test at a strain rate of 0.083 s^{-1} using notched and unnotched samples. As an example, the unnotched sample at $F = 0.3$ can sustain a stretch of 10 times its original length without rupture, and the notched sample is notch-insensitive, becoming blunted and remaining stable at the notch tip until a stretch of nearly 4 times its original length (**Figure 3g, 3h** and **Movie S1**). Similar to the work of extension, the fracture energy of the sample also increases with increasing F , and reaches a maximum value of 20 kJ/m^2 around $F = 0.4$, and decreases at high F (**Figure 3i**).

To further elucidate the tough mechanism of elastomer, cyclic tensile test was performed at $F = 0.3$. As shown in **Figure 4a**, the sample shows a large hysteresis for the first loading-unloading cycle at a maximum stretch ratio of 3, and a notable residual strain is observed after the unloading. It is noticed that the sample shows a distinct yielding at small deformation and a plateau in stress-strain relationship after yielding upon stretching to large deformation. To observe the stress distribution upon stretching of elastomer during the deformation, a homemade circular polarizing optical system combined with tensile tester was used to track the shape and isochromatic images under different deformation, which are

shown in **Figure S5**. From the initial start deformation to the yielding strain (0.23) and fracture strain (6.2), the stress was gradually increased and distributed homogeneously in the deformation part of the sample, as revealed by the color of the isochromatic images. In accompanying with the shape and stress change upon stretching, the sample does not show the necking-propagation phenomena although the stress-strain curve shows a remarkable yielding behavior. Moreover, to investigate whether the internal structure change is permanent or self-recoverable, the repeated cyclic tensile tests for the same samples were performed with different waiting times between two successive loading and unloading curves. The successive loading–unloading curve gradually recovers back to the first loading–unloading curve with the increase of the waiting time, indicating that interaction between molecular chain can reversibly break and reform. It was found that the tensile stress-strain curve almost overlaps to its original one after a waiting time of 90 mins. **Figure 4b** shows the waiting time dependence of the self-recovery ratio (hysteresis ratio) that was the area ratio of the second hysteresis loop to the first. The hysteresis ratio can reach 100%, and the sample shows fully self-recovery behavior after a waiting time of 90 mins. The large hysteresis indicates the energy dissipation required to break the interaction between the chain segments, while the topological constrain of the whole chains keeps integrity of sample, enabling the quick and fully self-recovery behavior. Furthermore, the short relaxation time of the chain segment gives rise to the high mobility of polymer chains, rendering the chain diffuse each other across the fracture surface when the sample is cut. Therefore, two pieces of cut elastomers can be healed at room temperature without any external stimulation. For example, the dumbbell sample with $\tau_0 = 4.0 \times 10^{-2}$ s at $F = 0.3$ was cut into two pieces using a razor blade, and one of them was dyed in light yellow for visualization (**Figure 4c**). Then, the two damaged halves were brought into contact. As a result, the sample self-healed at room temperature immediately even if the sample has a high Young's modulus ≈ 27 MPa. The joint between the two blocks is strong enough, which allows us to quantitatively evaluate the self-healing performance by tensile test. The tensile stress–strain curves of the virgin and healed samples after 24 h healing are presented in **Figure 4d** and Movie S2. Although the healed sample is weaker than the virgin sample, the strength of healed sample is still very

high (fracture strength: 1.6 MPa; fracture strain: 3.7 mm/mm), and the healing efficiency of the sample, defined as the ratio of fracture strain for the mended sample to the virgin sample, can reach as high as 47.6%. Therefore, when the mended sample with cross area of 3 mm² is loaded with a weight of 200g, it shows a negligible deformation without fracture for a long time (**Figure 4c**).

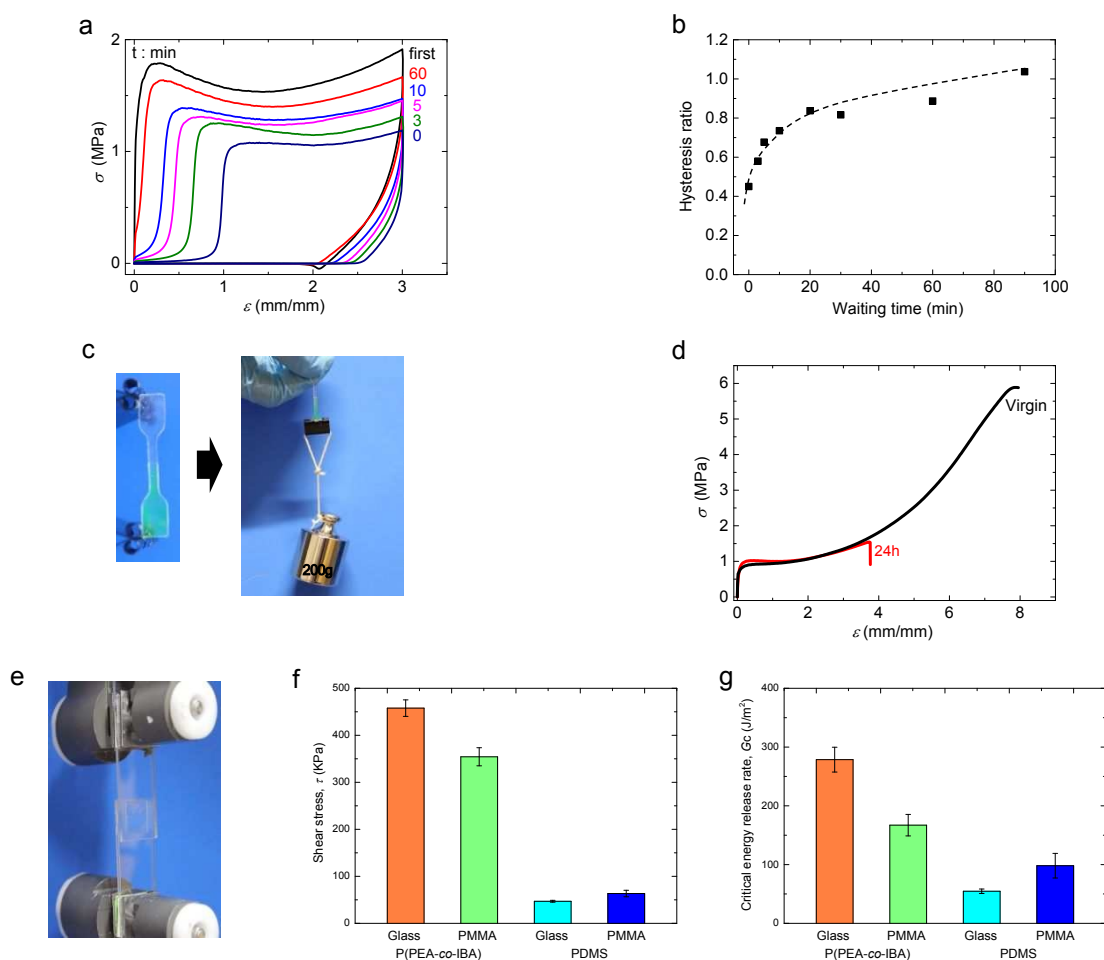


Figure 4. Self-recovery, self-healing and adhesive behavior of elastomers P (PEA-co-IBA) at $F = 0.3$. **(a)** self-recovery of the elastomer under different waiting times performed by cyclic tensile tests. The stretch strain rate is 0.14 s⁻¹. Data shown in the Figure 4a are the waiting times. Different specimens were used for different waiting times. **(b)** Waiting time, t , dependence of the hysteresis ratio which describes the area ratio of the second hysteresis loop to the first. **(c)** Demonstration of self-healing behavior of elastomers. The sample of dumb bell shape was cut into two pieces, and one piece was dyed in brilliant green. Then the cut surfaces of the two pieces were connected in air for several mins. The mended sample with cross section area of 3 mm² was

able to sustain a load of 200g. **(d)** Stress-strain curves of the virgin sample and mended sample. The self-healing experiment was performed at 25 °C for 24h. The stretch strain rate is 0.14 s⁻¹. **(e)** Lap-shear test to measure the adhesive behavior of elastomer on glass substrate. **(f)** Average shear stress of the elastomer and PDMS on glass and PMMA substrates and **(g)** critical energy release rate G_c of shear adhesive joints on these two different substrates.

Furthermore, the high mobility of polymer chains also affords the elastomers to adhere on the solid substrates. To quantitatively characterize the adhesive behavior, we used the lap-shear test to measure the adhesive strength of copolymer P(PEA-*co*-IBA) ($F = 0.3$) on glass and polymethylmethacrylate (PMMA) (**Figure 4e**). The average shear stress on different substrates are shown in **Figure 4f**. Compared with the soft poly(dimethylsiloxane) (PDMS), although P(PEA-*co*-IBA) ($F = 0.3$) is much stiffer, the adhesion to glass and PMMA substrates is much stronger. The critical energy release rate, G_c , characterized the interface strength of the joints, can reach as high as $\sim 280\text{J/m}^2$ when the elastomer adheres the glass substrate (**Figure 4g**). Such good adhesive properties indicate that the tough and transparent elastomer have a high potential to be used as soft matrix for glass fabric composites, as glue for flexible electro device.

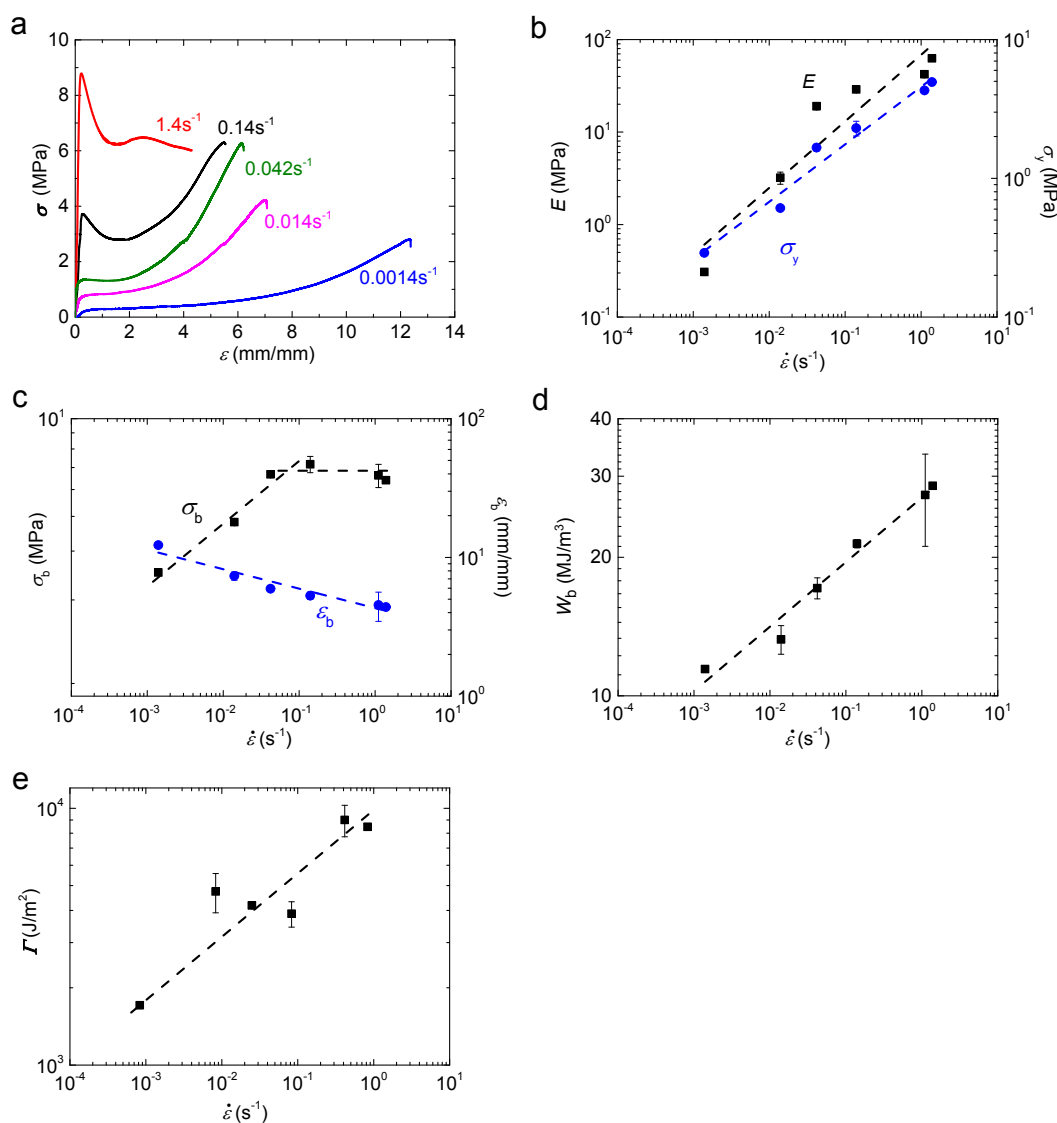


Figure 5. Mechanical behaviors of P(PEA-co-IBA) elastomers at varied strain rates $\dot{\epsilon}$. (a) Tensile stress-strain curves measured at different initial strain rates for sample of $F = 0.3$; (b) Strain rate dependence of Young's modulus E and yield stress σ_y ; (c) Strain rate dependence of fracture stress σ_b and fracture strain ϵ_b ; (d) Strain rate dependence of the work of extension to fracture W_b ; (e) Fracture energy Γ of sample ($F = 0.2$) measured by single-edge notch test at various strain rates. The sample with $F = 0.3$ is too tough to measure Γ at high strain rate, so sample with $F = 0.2$ was used. The dotted lines are guides for the eye.

The effect of viscoelasticity on the strength and toughness of the elastomers is further observed by tensile tests at varied strain rates. We performed tensile tests on the sample of F

= 0.3 at different strain rates, $\dot{\epsilon}$, in a range of nearly three orders of magnitude from 0.0014 to 1.4 s⁻¹, which corresponds to the viscoelastic transition regime of the sample observed in the linear rheological test (**Figure S3c**). Typical stress-strain curves are depicted in **Figure 5a**. The tensile mechanical behavior strongly depended on the applied strain rate. At extremely slow strain rates (~ 0.0014 s⁻¹), the sample was very soft and stretchable as most chain segments were relaxed; at intermediate strain rates, from 0.0014 to 0.14 s⁻¹, the chain segments are dynamic, and thus distinct yielding was observed, which substantially enhances the toughness of the sample; at extremely high strain rates (> 1.4 s⁻¹), the chain segments cannot relax, and the sample became stiff and brittle. The Young's modulus, E , yielding stress, σ_y , fracture stress, σ_b , fracture strain, ϵ_b , and work of extension, W_b of elastomers at various $\dot{\epsilon}$ are summarized in **Figure 5b, c and d**, respectively. The Young's modulus shows a strain rate dependence $E \sim \dot{\epsilon}^{0.5}$ which is consistent with the shear modulus that shows an angular frequency dependence of $G' \sim \omega^{0.5}$ in the rubbery-glassy transition regime. The yielding stress, σ_y , also shows a strain rate dependence similar to that of the modulus $\sigma_y \sim \omega^{0.5}$. Compared with the modulus results for small deformation, the polymers show relatively weak strain rate dependence at large deformation over similar observation time scales, including σ_b , ϵ_b and W_b . We consider that two reasons lead to the weak strain rate dependence of large deformation behavior. One is that at large deformation the true strain rate, defined as v/L , decreases with the increase of deformation. The true strain rate at fracture, given by $v/L_0(1 + \epsilon_b)$, was far lower than the initial strain rate v/L_0 , which may fall in or be close to the rubbery elastic region. Here, v , L_0 , and L are the stretch velocity, initial gauge length, and current gauge length, respectively. The other reason is that at large deformation the polymer network is subjected to large stress, which reduces the energy barrier required for the motion of chain segments. Thus, most chain segments become relaxed at such high deformations, and the mechanical behavior does not change with the strain rate.

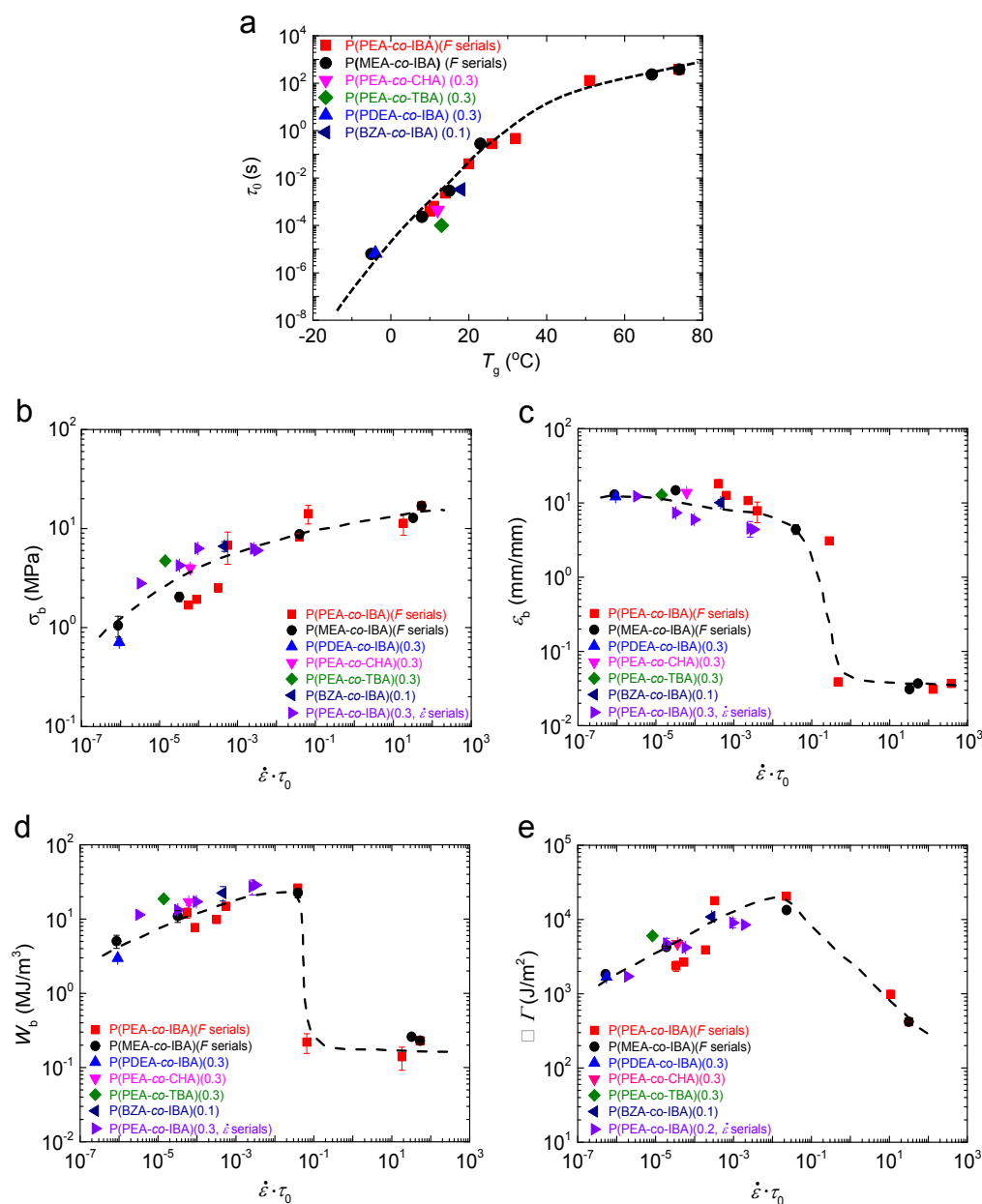


Figure 6. Summarized results for all the samples synthesized in this work. (a) Logarithmic plot of τ_0 and T_g . The dotted lines are guides for the eye. (b-e) Master curves of mechanical performance versus $\dot{\epsilon} \cdot \tau_0$. (b) Fracture stress σ_b ; (c) Fracture strain ϵ_b ; and (d) Work of extension to fracture W_b , from tensile test; (e) Fracture energy Γ from single-edge notch test. In (b-d), different colors of the data plots show P(PEA-co-IBA) with various F , P(MEA-co-IBA) with various F , P(PDEA-co-IBA) ($F = 0.3$), P(PEA-co-CHA) ($F = 0.3$), P(PEA-co-TBA) ($F = 0.3$), P(BZA-co-IBA) ($F = 0.1$) at the strain rate of 0.14 s^{-1} ; P(PEA-co-IBA) ($F = 0.3$) at different

$\dot{\epsilon}$. In (e), different colors of the data plots show P(PEA-*co*-IBA) with various F , P(MEA-*co*-IBA) with various F , P(PDEA-*co*-IBA) ($F = 0.3$), P(CHA-*co*-IBA) ($F = 0.3$), P(TBA-*co*-IBA) ($F = 0.3$), P(BZA-*co*-IBA) ($F = 0.1$) at strain rate 0.083s^{-1} ; P(PEA-*co*-IBA) ($F = 0.2$) at different $\dot{\epsilon}$.

To verify whether the determined polymer dynamics that control the mechanical behavior of the amorphous polymers are universal, we replaced the monomer PEA by ethylene glycol methyl ether acrylate (MEA), and synthesized a series of copolymers P(MEA-*co*-IBA) from monomers MEA and IBA, with varied molar fraction, $F = [\text{IBA}]/([\text{MEA}] + [\text{IBA}])$. The methyl side group in MEA has a weaker steric effect than that of phenyl groups in PEA (**Scheme 1**). The T_g of the homopolymer PMEA ($-34\text{ }^\circ\text{C}$) is much lower than that of PPEA ($10\text{ }^\circ\text{C}$). Master curves of the dynamic rheological spectra for these P(MEA-*co*-IBA) copolymers of varied F were constructed (**Figure S6**) using horizontal shift factors (**Figure S7**). P(MEA-*co*-IBA) copolymers also showed typical mechanical behaviors of amorphous polymers. Specifically, the PMEA exhibits rubbery behavior without crossover of G' and G'' over the entire observed frequency range (**Figure S6a**). With increasing F , the crossover of G' and G'' starts to appear at high frequency, and at $F > 0.3$, we observed the rubbery-glassy transition in the observation window (**Figure S6b-h**). As shown in **Figure 2d**, τ_0 of P(MEA-*co*-IBA) also shows a logarithmic increase similar to P(PEA-*co*-IBA) systems. Due to the lower steric effect of the MEA, at low IBA fraction ($F < 0.5$), P(MEA-*co*-IBA) samples have much lower τ_0 and T_g than those of P(PEA-*co*-IBA) at the same F (**Figure 2d** and **2e**). τ_0 nearly overlapped when F is larger than 0.5, independent of the chemical structures. This indicates that the dynamics of both series of the copolymers are dominated by IBA at large F . It is interesting to observe that the correlations between τ_0 and T_g for the two series of copolymers fall on the same logarithmic line (**Figure 2f**), which suggests that these two parameters are intrinsically related, independent of the specific chemical structures.

The differences in τ_0 leads to their different mechanical responses at the same fraction F (**Figure S8**). The P(MEA-*co*-IBA) system has lower modulus (**Figure 3c**), smaller fracture stress (**Figure 3d**) and work of extension to fracture (**Figure 3f**), but slightly larger fracture elongation (**Figure 3e**) than that of the P(PEA-*co*-IBA) system at small fraction of F ($<$

0.5), while at high F (> 0.5), the P(MEA-*co*-IBA) system shows almost the same behaviors as the P(PEA-*co*-IBA) system. The fracture energy of P(MEA-*co*-IBA) elastomers also increased with F and reached a maximum value at $F = 0.5$, which is slightly lower than that of P(PEA-*co*-IBA) ($F = 0.4$) (**Figure 3i**).

More copolymers from monomers di(ethylene glycol) ethyl ether acrylate (DEEA), 2-(2-phenoxyethoxy) ether acrylate (PDEA), and benzyl acrylate (BZA) as low T_g components, and cyclohexyl acrylate (CHA) and tert-butyl acrylate (TBA) as high T_g components as shown in **Scheme 1** were also synthesized. The rheological behaviors and the tensile behaviors of P(DEEA-*co*-IBA) ($F = 0.3$), P(PDEA-*co*-IBA) ($F = 0.3$), P(PEA-*co*-CHA) ($F = 0.3$), P(PEA-*co*-TBA) ($F = 0.3$), and P(BZA-*co*-IBA) ($F = 0.1$) are shown in **Figure S9** and **Figure S10**, respectively. The results of τ_0 , T_g , and mechanical properties are summarized in **Table S2**. Here we see again that τ_0 and T_g are correlated for different monomer combinations, which also fall on the same logarithmic line of previous two series of copolymers (**Figure 6a**). The mechanical performance of these copolymers strongly depends on their chemical structures at the same F and strain rate ($= 0.14 \text{ s}^{-1}$). For example, when the monomer with phenyl groups is changed from PEA to the more flexible monomer PDEA, the combination consisting of PDEA and IBA forms a soft and stretchable elastomer P(PDEA-*co*-IBA) ($F = 0.3$) with a low elastic modulus of 0.12 MPa, fracture stress of 0.71 MPa, work of extension of 2.97 MJ/m^3 , and a high fracture strain of 12.11 mm/mm. On the other hand, when the end side group of the monomer PDEA is changed from phenyl to methyl, the combinations of DEEA and IBA form a very soft and stretchable elastomer P(DEEA-*co*-IBA) ($F = 0.3$). The sample shows an extremely low elastic modulus of 0.042 MPa, fracture stress of 0.25 MPa, and work of extension of 0.87 MJ/m^3 . Furthermore, we also observed a tendency that the copolymers with the shorter relaxation time, τ_0 , show the higher self-healing efficiency (**Table S2**). For example, the elastomer P(PDEA-*co*-IBA) ($F = 0.3$) with a shorter τ_0 ($6.6 \times 10^{-6} \text{ s}$) shows a higher self-healing efficiency ($\sim 69.6\%$) than that of elastomer P(BZA-*co*-IBA) ($F = 0.3$) ($\sim 37.0\%$) with a longer τ_0 ($3.3 \times 10^{-3} \text{ s}$). This is understandable since that most of polymer chains are in the very mobile state for the sample

of shorter τ_0 , favoring the chain diffusing across the fractured surface and participating in the self-healing process.

To verify the universality of the dynamic effects at small deformation that control the mechanical performance at large deformation, we plot the fracture stress, σ_b , fracture strain, ε_b , work of extension, W_b , and fracture energy, Γ , against the parameter $\dot{\varepsilon} \cdot \tau_0$ for all the experimental data in **Figure 6b-6e**, including varied F at the same $\dot{\varepsilon}$, and varied $\dot{\varepsilon}$ at the same F from the results of **Figure 3**, **Figure 5**, **Table S1** and **Table S2**. The quantity $\dot{\varepsilon} \cdot \tau_0$ represents the relative deformation rate to the dynamics of the Kuhn segment. We see that all the data roughly fall on master curves for each parameter over ten orders of magnitude of $\dot{\varepsilon} \cdot \tau_0$ from 10^{-7} to 10^3 . These results indicate that the mechanical properties of elastomers at large deformation are indeed dominated by the dynamic effect of chain segments, independent of the specific chemical structures and experimental conditions. The fracture stress shows an increasing trend with $\dot{\varepsilon} \cdot \tau_0$ (**Figure 6b**), while the fracture strain exhibits an abrupt decrease around $\dot{\varepsilon} \cdot \tau_0 \approx 0.1$ (**Figure 6c**), indicating that the elastomers become brittle at the glassy regime. The elastomers increase in toughness with increasing $\dot{\varepsilon} \cdot \tau_0$ until the critical value at $\dot{\varepsilon} \cdot \tau_0 \approx 0.1$. Above this critical value, the toughness abruptly decreases. As the relaxation time related to the Rouse motion of entangled strands, τ_e , is about $10^3 \sim 10^4$ times of the Kuhn monomer segment relaxation time, τ_0 , we see that the critical strain rate, where the toughness reaches a maximum value, is much higher than the corresponding frequencies of $1/\tau_e$ (**Table S1**). Furthermore, the critical strain rate is also higher than the peak frequency of $\tan\delta = G''/G'$ (**Table S1**). This is quite different from common intuitive expectation that the maximum toughness should be observed when the strain rate reaches the peak frequency of $\tan\delta$. The results clearly show that the materials reach a maximum toughness in the rubbery-glassy transition region where the materials are strongly viscoelastic. It also indicates that we can develop tough soft materials by designing the Kuhn monomer segment relaxation time to be 10 times faster than the experimental observation time.

Finally, we compare the mechanical performance of the elastomers developed in this work with other soft materials. Ashby plots of fracture energy versus Young's modulus, $\Gamma \sim E$, and fracture stress versus Young's modulus, $\sigma_b \sim E$, of our elastomers and other polymers, especially the recently developed room temperature self-healing elastomers, are presented in **Figure S11**. Although our elastomer is amorphous without specific physical interactions, with appropriate chemical structure and optimization, these elastomers also exhibit high strength (8.25 MPa), stiffness (294 MPa) and toughness (20 kJ/m²) at room temperature. These results demonstrate that the mechanical performances of our elastomers are tougher than the reported elastomers from the acrylate polymers, and comparable with the toughest natural rubbers and most of room temperature self-healing elastomers. To demonstrate the excellent mechanical performance of the elastomers, we interlocked an elastomer sheet P(PEA-*co*-IBA) ($F = 0.3$) and a natural rubber sheet with the same geometry (12×2×1 mm³), and stretched them in a tensile tester (**Movie S3**). During stretching, the natural rubber elongated and then fractured, while the elastomer was undamaged, demonstrating that the elastomer is stronger than the natural rubber.

3. Conclusions

We can synthesize tough, self-healing and adhesive elastomers by one-step bulk polymerization of acrylate monomers without using organic solvents. By copolymerization of acrylate monomers with contrasting Kuhn segment relaxation times, the dynamics of the elastomers are tunable over a wide range up to six orders in magnitude. The dynamic effect of the chain segment dominates the mechanical performance of amorphous polymeric materials. The materials of diverse chemistry and composition show a universal tough-brittle transition at a critical strain rate, $\dot{\epsilon} \cdot \tau_0 \approx 0.1$, due to the rubbery-glassy transition. Highly tough soft materials can be achieved when the Kuhn segment relaxation time, τ_0 , of the material is designed to be 10 times faster than the observation time. Furthermore, the copolymer with short Kuhn segment relaxation times afford the quick polymer diffusion across the fractured surfaces after cutting, and therefore the elastomers show the high self-healing ability. The high mobility of polymer chains also affords the elastomers to strongly

adhere on the different solid substrates. Owing to the simple synthesis, wide dynamic tunability, toughness, self-healing and adhesion, the novel elastomers developed in this work significantly increases the choice of elastomers for numerous real applications. The excellent adhesion of the materials makes them excellent candidate as soft and energy dissipative matrix for fiber-reinforced tough composites. The universal ductile-brittle transition behaviors observed in this work will give insight to design novel advanced elastomers with excellent mechanical properties based on the dynamics of linear rheology.

4. Experimental section

Chemical reagents. The monomers, di(ethylene glycol) ethyl ether acrylate (DEEA), ethylene glycol methyl ether acrylate (MEA), 2-(2-phenoxyethoxy) ether acrylate (PDEA), ethylene glycol phenyl ether acrylate (PEA), benzyl acrylate (BZA), cyclohexyl acrylate (CHA), tert-butyl acrylate (TBA), and isobornyl acrylate (IBA) were supplied by Osaka Organic Chemical Industry Ltd, Japan, and were used without further purification. Ultraviolet initiator, benzophenone (BP, KANTO Chemical Co., Inc.) was used as received. The SYLGARD 184 silicone elastomer (Fujifilm Wako Pure Chemical Co.) was used without further purification.

Synthesis of elastomers. The elastomers were synthesized from the random copolymerization of two monomers, one with T_g of its homopolymer lower than, and the other with T_g of their homopolymers higher than the room temperature (24 °C) (**Scheme 1**). The mixed liquid containing total monomer concentration (≈ 5.2 M) with molar fraction F of the high T_g monomer and 0.0052 M ultraviolet initiator, benzophenone was injected into the rectangular mold consisting of a pair of glass plates that were separated by a fluoro-elastomer spacer with 1.5 mm-thickness. The polymerization was carried out in argon atmosphere (oxygen concentration < 0.1 ppm) under the UV light (UVP lamp Toshiba-FL15BLB, wavelength 365 nm, light intensity $\sim 4\text{mWcm}^{-2}$) irradiated from the two sides of the glass mold for 10 h. The polymers thus obtained have a relatively high molecular weight but large dispersity, as revealed by Gel Permeation Chromatography. For example, the molecular weight and

molecular weight distribution of the sample P(PEA-*co*-IBA) is about 2.5×10^5 g/mol and 4.1, respectively, when the total monomer concentration (2 M) with molar fraction of 0.3 was used to synthesize the elastomers.

ACKNOWLEDGMENTS

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Author information

L. Chen and T. L. Sun equally contributed to this work.

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Title: Facile Synthesis of Novel Elastomers with Tunable Dynamics for Toughness, Self-healing and Adhesion

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Self-healing and Adhesion

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Table of contents entry :

We propose a universal strategy to design novel advanced elastomers with excellent properties through dynamic linear rheology.

ToC figure

