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Synthesis of polyurethane/vinyl polymer hybrids with unexpected mechanical properties using a macro chain transfer agent†

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Polyurethane is one of the most essential polymer materials due to its wide range of applications in the forms of elastomer and foam. We here report the synthesis of customized polyurethane by hybridization with vinyl polymer using a polyurethane-based macroinitiator and successive radical polymerization. First, we performed step polymerization of a trithiocarbonate-containing diol, bis{4-[ethyl-(2-hydroxyethyl)carbamoyle]benzyl}trithiocarbonate, and isophorone diisocyanate to afford the polyurethane-based macroinitiator (PU-TTC: $M_n = 27.0 \times 10^3$; $M_n/M_w = 1.71$) for reversible addition-fragmentation chain-transfer (RAFT) radical polymerization of vinyl monomers. We demonstrated polymerization of styrene and methyl methacrylate mediated by PU-TTC as the macro chain transfer agent to prepare a hybrid consisting of polyurethane and poly(styrene) or poly(methyl methacrylate). Compared to the methacrylate homopolymer, differential scanning calorimetry of the polyurethane hybrid showed improved thermal properties and tensile strength tests revealed unusual elongation behavior.

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1. Introduction

The high performance of polymer materials has contributed to many applications not only in academia, but also in industrial fields. Among such materials, polyurethanes have fascinated polymer chemists because of their unique elastic properties and high thermal and chemical stabilities. Syntheses of commercially available polyurethanes are usually performed by step polymerization of bisphenol A and several diisocyanates including isophorone diisocyanate (IPDI).^{1–5} But recent urgent concerns about environmental pollution have promoted the exploration of the use of alternative chemicals instead of bisphenol A. However, a promising alternative synthetic approach that retains the conventional performance of polyurethane has not been reported.

One of the evolving ideas is the hybridization of polyurethane and vinyl polymers.^{6,7} As the miscibility of a mixture of polyurethanes and vinyl polymers is extremely low,⁸ a reversible addition-fragmentation chain-transfer (RAFT) approach to well-defined telechelic vinyl polymers with hydroxyl terminals as polymeric diol-type building blocks (macromonomer) for polyurethanes was developed by Sudo *et al.*⁹ An alternative synthetic strategy of direct incorporation of vinyl monomer into a polyurethane backbone is worth considering because the reactivity

of a macromonomer needs to be generally low for the step polymerization to obtain a desirable molecular weight.¹⁰ Our survey showed that the RAFT approach to synthesize multiblock vinyl polymers had been reported,^{11,12} but there is only one report dealing with polyurethane-based macroinitiators.¹⁰ In this report, we demonstrate RAFT radical polymerization using a polyurethane-base macroinitiator, prepared *via* step polymerization of bis{4-[ethyl-(2-hydroxyethyl)carbamoyle]benzyl}trithiocarbonate (TTCOH) and IPDI. Using this macroinitiator, poly(styrene) [poly(St)] and poly(methyl methacrylate) [poly(MMA)] segments are incorporated into the polyurethane backbone. We also investigated the thermal and mechanical properties of the resulting hybrid. We found an unexpected result that poly(MMA) incorporated into the macroinitiator appeared to be more ductile, compared with poly(MMA) prepared using a conventional RAFT agent.

2. Experimental section

2.1. Materials

Styrene (St), methyl methacrylate (MMA), tris(2-phenylpyridinato)iridium(III) [Ir(ppy)₃] (purified by sublimation), isophorone diisocyanate (IPDI), 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) were purchased from Tokyo Chemical Industry Co., Ltd (Tokyo Japan). Bis{4-[ethyl-(2-hydroxyethyl)carbamoyle]benzyl}trithiocarbonate (TTCOH), dibutyltin(IV) dilaurate (DBTDL), *N,N*-dimethylformamide (DMF) (deoxidized) were purchased from Wako Pure Chemical Industries, Ltd (Osaka Japan). Acetone, tetrahydrofuran (THF), hexane, and methanol were purchased from Nacalai

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Tesque Co., Ltd (Kyoto, Japan). MMA was distilled under reduced pressure under a nitrogen atmosphere. St was purified by passing through a basic alumina column.

2.2. Synthesis of polyurethane containing the trithiocarbonate moiety (PU-TTC)

All operations were carried out in a glove box, and the flasks were flushed with dry nitrogen. TTCOH (395.8 mg, 0.76 mmol), IPDI (168.9 mg, 0.76 mmol), and DMF (1.00 mL) were premixed at room temperature, then DMF solution of DBTDL was added and heated to 60 °C for a predetermined time. The reaction mixture was quenched with methanol and the synthesized polymers were purified using THF and acetone/water (1/2 v/v) as good and poor solvents, respectively. The products were dried at 50 °C under reduced pressure.

2.3. RAFT polymerization of MMA or St with PU-TTC as macro chain transfer agents

All operations were carried out in a glove box, and the flask were flushed with dry nitrogen. PU-TTC (18.6 mg, 0.025 mmol trithiocarbonate unit), MMA (750.9 mg, 7.5 mmol) or St (781.1 mg, 7.5 mmol) were dissolved in DMF (1.02 mL) in a flask and Ir(ppy)₃ was added at 15 ppm (mol/mol) relative to the monomer. The polymerization was performed under blue-LED irradiation (456.1 nm, 15.04 lm W⁻¹, D160 series 24V 10 mm LED dot type, JW-system Co. Ltd) at room temperature. After a predetermined time, polymerization was quenched by stopping the blue-LED irradiation. The synthesized polymers were purified by reprecipitation using THF as good solvent and methanol [for poly(MMA)] or hexane [for poly(St)] as poor solvents. The products were dried at 50 °C under reduced pressure.

For the polymerization without blue-LED irradiation, AIBN was dissolved in a flask at a ratio of trithiocarbonate unit/AIBN = 1/0.2 (mol/mol) and magnetically stirred at 70 °C for a predetermined time.

2.4. Synthesis of MMA homopolymer

As a control sample, MMA homopolymer was synthesized by RAFT polymerization. All operations were carried out in a glove box, and the flask flushed with dry nitrogen. TTCOH (13.0 mg, 0.025 mmol), MMA (1251.5 mg, 12.5 mmol) were dissolved in deoxidized DMF (4.90 mL) in a flask and AIBN was added at a ratio of TTCOH/AIBN = 1/0.2 (mol/mol) and magnetically stirred at 70 °C. After 24 h, the synthesized polymers were purified using THF as a good solvent and methanol as a poor solvent. The product was dried at 50 °C under reduced pressure.

2.5. Photodegradation of polyurethane–poly(MMA)

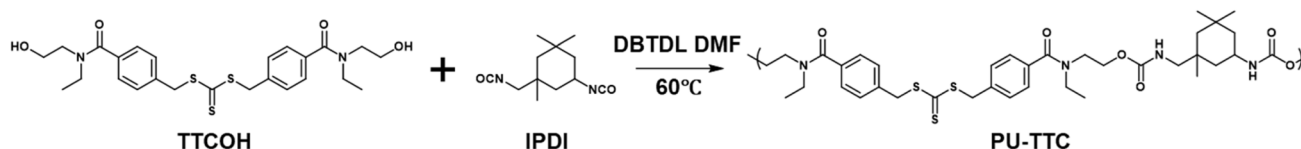
Reprecipitated polyurethane–poly(MMA) (10 mg), DMF (0.5 mL) and hydroquinone (1.0 mg) were mixed in a flask. The sample was exposed under a UV lamp (365 nm, 41 mW cm⁻², MAX-303, Asahi spectra) at room temperature for 14 hours. The solution was withdrawn for SEC measurements without reprecipitation.

2.6. Characterization

¹H NMR (400 MHz) spectra were acquired using a Bruker Analytik DPX400 at 27 °C. FT-IR spectra (KBr disc method) were acquired using a FT/IR-6600 spectrometer (JASCO). The number average molecular weight (M_n) and polydispersity (M_w/M_n) values of the products were assessed using a size exclusion chromatography (SEC) system, which included a PU-4185 semi-micro pump (JASCO) that was connected to an RI-4035 differential refractometer (JASCO) and a CO-2065 Plus Intelligent column oven (JASCO) equipped with a TSK-gel SuperMultipore HZ-M columns (TOSOH) was used. The measurement conditions were THF as eluent, 40 °C, flow rate of 0.35 mL min⁻¹ and sample concentration of 1 mg mL⁻¹. Poly(methyl methacrylate) standards were used for calibration. Differential scanning calorimetry (DSC) experiments were performed using a DSC7020 (HITACHI) system. The first heating was carried out from 30 °C to 200 °C. The temperature was then lowered to -40 °C. The second heating was carried out from -40 °C to 200 °C. The temperature change rate was set at 10 °C min⁻¹. All measurements were performed under nitrogen gas flow. The tensile tests were performed using an AGS-500NX (SHIMADZU) apparatus. In carrying out the tests, dogbone-shaped samples with length of 13 mm and width of 4 mm were prepared using a cutting die. The tests were carried out at room temperature at an elongation rate of 10 mm min⁻¹. Scanning electron microscopy (SEM) was performed using a JSM-7800F (JEOL) machine. Specimens coated with platinum palladium at a thickness of 5 nm were attached to carbon tape. The acceleration voltage was set at 5 kV.

3. Results and discussion

According to Scheme 1, step polymerization, using 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) and dibutyltin(IV) dilaurate (DBTDL) as catalysts, of commercially available TTCOH and IPDI was performed at 60 °C to give polyurethane containing trithiocarbonate (PU-TTC) moieties. In both cases, the expected step polymerizations proceeded to give viscous polymeric materials after the reaction. NMR measurements (Fig. S1–S3†) showed no presence of remaining monomer and fitted the expected spectrum of the PU-TTC product. The structure of the PU-TTC product was confirmed by IR (Fig. S4†). Characteristic



Scheme 1 Synthesis of polyurethane with trithiocarbonate unit (PU-TTC).



Table 1 Synthesis and characterization of synthesized PU-TTC^a

Run	Catalyst	[Cat.] ₀ /[M] ₀	Time (h)	M_n^b (kg mol ⁻¹)	M_w/M_n^b	Repeat unit
1	TBD	5 mol%	48	5.78	2.63	7.8
2	DBTDL	6.6 mol%	24	27.0	1.68	36
3	DBTDL	6.6 mol%	48	27.0	1.71	36

^a Reaction temperature = 60 °C, in DMF (deoxidized). ^b Determined by SEC with poly(methyl methacrylate) standards.

peaks at 3318 cm⁻¹ (NH stretching), 1716 cm⁻¹ (C=O stretching of the urethane group), and 1535 cm⁻¹ (NH vibration) were observed in the IR spectrum, suggesting the formation of urethane bonds, and also a peak around 1620 cm⁻¹ attributed to C=O stretching of the TTCOH unit was observed. These results confirmed the synthesis of our expected polyurethane containing a trithiocarbonate structure.

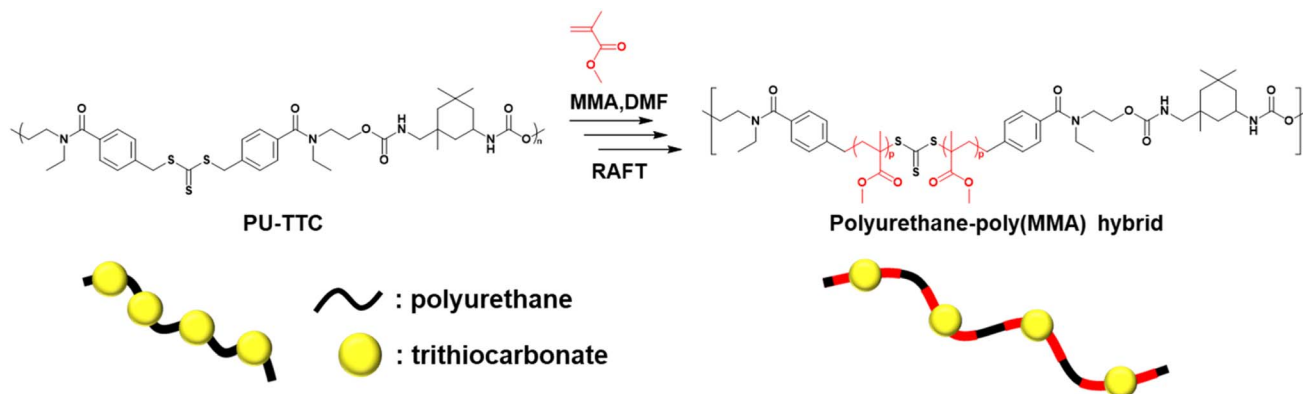
The details of the reaction results are summarized in Table 1, in which it seems that DBTDL is a superior catalyst (runs 2 and 3), similar to results seen in other polyurethanes syntheses.^{13–15} For these runs, the number average molecular weight (M_n) and polydispersity a (M_w/M_n), estimated by SEC measurements calibrated using poly(MMA) standards, M_n were 2.7×10^4 for both runs and M_w/M_n s were 1.68 and 1.71, respectively for runs 2 and 3.

Subsequently, styrene monomer was incorporated into the PU-TTC backbone under blue-LED irradiation (Scheme 2 and run 1 in Table 2). The polyurethane-based macroinitiator acted at room temperature and monomer consumption was confirmed from ¹H NMR, accompanied by a shift of the SEC results to higher molecular weights. After 48 h irradiation, the M_n (initially 27.0×10^3 for the parent macroinitiator) increased to 32.8×10^3 , accompanied by a broadening of M_w/M_n (from 1.71 to 2.91) (run 1 in Table 2). The broadening of M_w/M_n indicated that the RAFT radical polymerization was not a controlled polymerization.

MMA was also polymerized using PU-TTC as the macroinitiator in a similar procedure to St. After monomer addition of MMA ([M]₀: 2.0 M), blue-LED irradiation was performed at room temperature (run 2 in Table 2). The SEC trace characteristic of the macroinitiator ($M_n = 27.0 \times 10^3$, $M_w/M_n = 1.71$) shifted to

higher molecular weights ($M_n = 32.8 \times 10^3$), but without broadening of the polydispersity index ($M_w/M_n = 1.73$). The results revealed that the RAFT radical polymerization indeed proceeded in a controlled manner.

On the other hand, polymerization of MMA with AIBN as an alternative radical trigger was carried out instead of using blue LED irradiation. Heating at 70 °C produced polymerization similar to that seen under blue LED irradiation but showed a more marked increase in M_n and a broader polydispersity (runs 3–4 in Table 2 and Fig. S5†). This may be due to the cleavage of the main chain of PU-TTC by photolysis of the trithiocarbonate unit in RAFT polymerization with blue-LED, as reported by several groups.^{16,17} Actually, the correlation between the monomer conversion and number average molecular weight in RAFT polymerization by blue LED irradiation *via* PU-TTC was investigated (Fig. S6 and Table S1†). Although, the monomer conversion showed a linear increase with time, a decreasing trend in molecular weight was observed during the course of polymerization. This suggested that photolysis of trithiocarbonate occurred simultaneously with propagation reaction. Photolysis of trithiocarbonate unit is considered to have caused the main chain being cleaved and the formation of degradation products such as thioethers, which don't show RAFT polymerization activity, resulting in the polymerization being terminated while keeping low molecular weight and remaining the monomer. Low molecular weight tailing is also observed in the SEC trace after polymerization of MMA with AIBN, which means that the initiation of MMA was not regulated due to the bulkiness of the macro CTA, PU-TTC. Main chain scission was carried out by UV irradiation^{18–20} in the presence of hydroquinone in order to check that the



Scheme 2 RAFT polymerization of MMA using PU-TTC.



Table 2 RAFT polymerization of MMA using PU-TTC^a

Run	[M] ₀ /[TTC] ₀	[M] ₀ (mol L ⁻¹)	Radical trigger	Time (h)	Conv. ^b (%)	M _n ^c (kg mol ⁻¹)	M _w /M _n ^c	T _g (°C)
1 ^{d,e}	300	4.0	Redox-LED	48	48	32.8	2.91	98
2 ^d	300	2.0	Redox-LED	24	82	32.8	1.73	116
3 ^f	100	2.0	AIBN	24	80	79.8	2.20	118
4 ^f	300	2.0	AIBN	24	68	122.1	1.98	116

^a Polymerization using PU-TTC (run 3 in Table 1) as chain transfer agent. ^b Calculated from ¹H NMR in CDCl₃. ^c Determined by SEC with poly(methyl methacrylate) standards. ^d Polymerization with Ir(ppy)₃ as a redox catalyst by blue-LED irradiation. ^e Styrene was used as monomer. ^f Polymerization with AIBN as a radical trigger under 70 °C ([TTC linkage]/[AIBN] = 1/0.2).

polymerization proceeded in a radical fashion. As shown in Fig. S7,† after UV irradiation the SEC trace of polyurethane–poly(MMA) hybrid shifted to the low molecular weight region, indicating that the polymerization actually occurred in a radical manner. As shown in Schemes 1 and 2, it is expected that chain initiation is proposed here through C–S bond cleavage. Compared with ¹H NMR spectrum of parent PU-TTC (Fig. S8†), we could new ¹H NMR signal assigned to methylene protons adjacent to trithiocarbonate moiety at 2.3 ppm as the evidence of new C–S bond formation during polymerization of MMA (Fig. S9†), which is different from the corresponding methylene (at 4.6 ppm) of the parent PU-TTC (Fig. S8†).

Finally, we checked the thermal and mechanical properties of the polyurethane–vinyl polymer hybrids by DSC and tensile strength (Fig. 1) measurements, respectively. To compare thermal properties, MMA homopolymer poly(MMA) was synthesized *via* RAFT polymerization using TTCOH as the RAFT agent. The poly(MMA) polydispersity and M_n were estimated by SEC to be 1.98 and 172.6 × 10³, respectively. The DSC trace for the polyurethane–poly(MMA) hybrid (run 3 in Table 2) shows a heat capacity inflection point at 118.1 °C (T_g) (Fig. S10†). This is approximately 10 °C higher than that of the poly(MMA) (108.4 °C), and the T_g of the parent PU-TTC was observed at 4 °C (Fig. S11†), indicating improved thermal properties due to hybridization. The higher T_g value for the hybrid relative to that of the poly(MMA) is thought to be due to the formation of hydrogen bonds between the urethane groups (–NHCOO–)

present in the main chain and the carbonyl groups (C=O) of the MMA or amide groups (–NRCO–) derived TTCOH.

Although PU-PMMA hybrid looks transparent (Fig. 2), quantitative analysis of the transparency evaluated the transmittance at 590 nm showed 7%, which is much lower than that (86%) of PMMA homopolymer (Table S2†). The tensile strength of the hybrids was characterized by uniaxial elongation tests conducted at room temperature. Fig. 1 shows a comparison of the stress–strain curves of polyurethane–poly(MMA) hybrids with those of the MMA homopolymer as a control sample. The latter showed typical brittle fracture behavior, whereas the polyurethane–poly(MMA) hybrid exhibited ductile fracture behavior with a distinct yield point. The introduction of intermolecular interactions such as hydrogen bonds was expected to improve tensile strength, but the results showed opposite behavior with a Young's modulus of 1.6 GPa for the PMMA homopolymer, compared to 1.0 GPa for poly(urethane-MMA). The Young's modulus was calculated from the initial slope. It is noteworthy that in the polyurethane–poly(MMA) hybrid, elongation caused whitening near the fracture zone, as noted by others in a rubber–poly(MMA) composite.²¹ Hayashi *et al.*^{22,23} have already reported that such whitening in amorphous glassy polymers, polyester-*graft*-poly(MMA), is due to cavitation. Such whitening was not observed for the poly(MMA) homopolymer. As the cavitation phenomenon is known to usually produce a large amount of voids,²⁴ SEM observations of the samples after elongation were carried out (Fig. 2) to search for such voids. Many scattered voids (*ca.* 1 μm of diameter) were observed in the whitened region, whereas a uniform smooth surface was observed in other regions. Observations of the fracture surface were also performed, which revealed a dense porous surface. Furthermore, attention to the inside of the voids confirmed the formation of numerous fine fibrils. They were considered to have been formed by the elongation of voids, suggesting that the voids observed in this study were not generated during the forming process of the specimens, but were produced during the tensile test. The increased elongation at break may be due to more energy absorption caused by the formation of voids resulting from the preferential cleavage of physical crosslinking due to intermolecular hydrogen bonds in the urethane. The formation of hydrogen bonds was confirmed by IR measurements (Fig. S12†). Full range of the FT IR spectrum was also shown in Fig. S13.† A shoulder peak was observed in the peak derived from carbonyl stretching, which may be due to the overlapping absorptions of the free carbonyl (1727 cm⁻¹) and

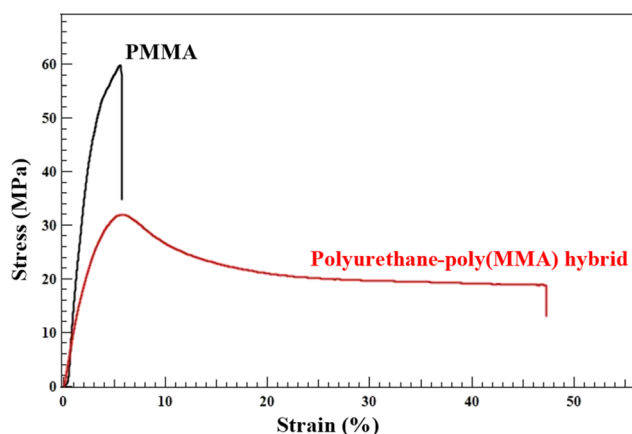


Fig. 1 Stress–strain curves of polyurethane–poly(MMA) hybrid (run 3 in Table 2) and MMA homopolymer (room temperature, 10 mm min⁻¹).



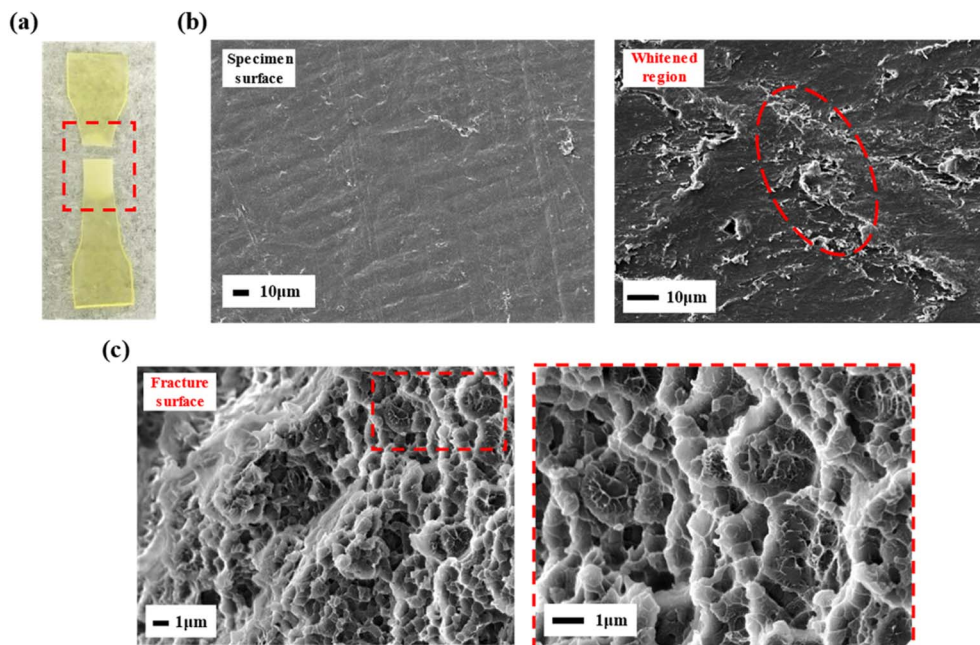


Fig. 2 (a) Fractured specimen of poly(urethane-MMA) (run 3 in Table 2). (b) SEM images of the transparent region and whitened region (0.1 mm from the edge) of the fracture piece. (c) SEM images of the fracture surface of the fracture piece.

hydrogen bonded carbonyl (1714 cm^{-1}), and a peak (1635 cm^{-1}) derived from hydrogen bonded esters was also observed,²⁵ indicating that the intermolecular hydrogen bonding formation is likely responsible. In view of the above results, the observation of the whitening phenomenon may indicate an increase in the toughness of polymeric materials, as cavitation can prevent the formation of crazes before they reach an unstable state that can cause macroscopic cracks. As a control, the parent polyurethane, PU-TTC, showed the excellent ductility as shown in Fig. S14,[†] in which PU-TTC showed over 400%. We now concluded that the improved ductility of polyurethane-PMMA hybrid is ascribed to the urethane linkages dispersed in the PMMA matrix.

4. Conclusion

In this paper, we demonstrated polymerization of styrene and methyl methacrylate mediated by PU-TTC as the macro chain transfer agent to prepare a hybrid consisting of polyurethane and poly(styrene) or poly(methyl methacrylate). Compared to the methacrylate homopolymer, polyurethane-poly(MMA) hybrid showed improved thermal properties and ductility in the tensile strength measurement. These fundamental results should activated the recent researches aiming at frontier materials including flexible coatings, impact-resistant films, or elastomeric actuators.

Data availability

The data supporting this article are available in the manuscript and the ESI.[†] Additional data can be obtained from the authors upon request.

Author contributions

Monomer and polymer synthesis, structural characterization, property investigation and manuscript preparation were performed by R. U.; data analyses and treatments were directed by A. T.; and guidance on manuscript writing, review and editing was provided by A. T.

Conflicts of interest

There are no conflicts of interest to declare.

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