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Synthesis and properties of readily recyclable polymers from bisfuranic terminated poly(ethylene adipate) and multi-maleimide linkers

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Abstract

Polymers that can repeatedly polymerize and depolymerize at moderate conditions was designed and synthesized. Furyl-telechelic poly(ethylene adipate) [PEA2F] was prepared and copolymerized with bis- and tris-maleimides by Diels–Alder [DA] reaction at 60 °C. Though the reaction with bismaleimide proceeded partially to give a polymer whose molecular weight was only twice as large as PEA2F, the reaction with trismaleimide gave a product with a 3D-network structure. The latter product shows elasticity at room temperature. By keeping at 145 °C, these DA products were easily disconnected by retro-Diels–Alder [rDA] reaction to reproduce the starting macromonomer, PEA2F. The repetition of the cycle of the DA and rDA reactions induce the reduction of neither the mechanical properties of the DA products nor the molecular weight of the rDA products. Therefore, we have successfully obtained readily recyclable polymers.

Keywords: Recyclable polymers; Diels–Alder reaction; Macromonomer

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1. Introduction

Reusable and recyclable polymeric materials are effective for waste prevention and conservation of petroleum resources. In order to construct sustainable society, materials design with optimization of recyclability is highly desired. One of the effective recycling processes of polymers is chemical recycle, in which polymeric materials are depolymerized into monomers by chemical or biological methods, and then, the monomers are repolymerized to reproduce the materials [1,2].

We will propose a molecular system for readily recyclable polymers in this study. The targets are polymers made from a macromonomer having two functional groups at both chain ends and di- and tri-functional linkers. The functional groups are selected so as to form reversible bonds that can connect and disconnect under mild conditions. The reversible bond can be used to construct the cycle of polymerization and depolymerization. This polymer can be easily recycled by depolymerization and repolymerization of the reversible bond. In general, the molecular weight of polymeric materials gradually decreases by external stress during use. In the target polymer system, the reversible bond, which is weaker than the other non-reversible bonds, would be selectively dissociate to preserve the structure of the macromonomer. So, the target polymer forms the recycle system with the minimum molecular degradation.

As a reversible reaction, Diels–Alder [DA] cycloaddition of diene and dienophile groups is selected. The advantages of the use of DA reaction are as follows: both the forward and retro DA reactions proceed under relatively mild condition, require no additives such as catalyst, and generate no by-products. There are several papers on the application of the DA chemistry to the construction of the backbone structure of linear polymers [3–10]. One of them considers the recyclability of the DA polymer [8]. The DA reaction is also used for the cross-linking of linear polymers [11–18]. Densely cross-linked polymers were also made from tetra-furan and multi-maleimide by DA reaction, [19,20] in which the authors focused on the remendability of these polymers. A cross-linked polymer with rewritable shape-memory was made from a star-shape telechelic poly(lactic acid) and tris-maleimide by DA reaction [21].

In this paper, we synthesize copolymers of bisfuranic terminated poly(ethylene adipate), PEA2F, with bismaleimide, 2M, and trismaleimide, 3M, and investigate the recyclability of these copolymers (Scheme 1). PEA2F is a linear macromonomer and 2M and 3M are 2- and 3-arm linkers, respectively. The advantage of the use of a macromonomer is that polymers with various properties can be designed by

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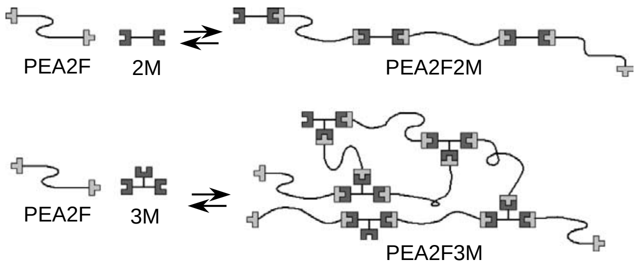


Scheme 1. Schematic representation of synthesis of readily recyclable polymers.

simply replacing the main chain of the macromonomer. We can expect that the resultant copolymer possesses characteristics similar to the parent macromonomer.

2. Experimental section

2.1. Materials

Furfuryl alcohol and acetic acid furfuryl ester were purchased from Tokyo Kasei Kogyo Co. Ltd. *N*-ethylmaleimide and tolylene 2,4-diisocyanate terminated poly(ethylene adipate) [PEA2Icn] (3 wt% isocyanate) were purchased from Kanto Kagaku and Aldrich, respectively. All the reagents and solvents were used as received. In the ^{1}H NMR spectrum of PEA2Icn, no peaks ascribed to the unmodified chain end of poly(ethylene adipate) were observed. So we have assumed that all the chain ends of this polymer were modified with isocyanate. 1,2-Bis(maleimide)ethane [2M] [22] and tris(2-maleimide ethyl)amine [3M] [19] were synthesized as previously reported.

2.2. Measurements

Four hundred MHz ^{1}H NMR spectra of solution samples were obtained on a JEOL JNM-AL400 spectrometer. Gel permeation chromatography (GPC) was carried out on a TOSOH HLC-8220GPC equipped with two Shodex GPC LF-804 columns. Polystyrene standards with low polydispersity were used to construct a calibration curve. Differential scanning calorimetry (DSC) were carried out on a PERKIN ELMER Pyris1 at a heating rate of 20 or −20 °C/min under N$_2$ atmosphere. For this analysis, the sample of ca. 9 mg were sealed in an aluminum pan. Mechanical properties of film samples were evaluated using a tensile testing machine, SHIMAZU EZ test, at a cross-head speed of 20 mm/min at room temperature. Sample films of $22\times5\times0.2\ \mathrm{mm}^3$ were used. Values of tensile strength, elongation at break, and tensile modulus were averaged over the data of at least five samples. IR spectra of cast film samples were recorded on a JEOL WINSPEC 100.

2.3. Model DA reaction

As a low molecular weight model of DA reaction, the reaction of furfuryl acetate and *N*-ethylmaleimide were selected. Equimolar amounts of furfuryl acetate and *N*-ethylmaleimide were mixed without solvents and stirred at a given temperature for a given time. Then the mixture was immediately dissolved in CDCl$_3$ at room temperature to stop the reaction. The reaction product was analyzed by ^{1}H NMR spectroscopy.

2.4. Synthesis of macromonomer, bisfuranic terminated poly(ethylene adipate) [PEA2F]

Under N$_2$ atmosphere, PEA2Icn (15.9 g/11.4 mmol NCO) was dissolved in 40 ml of dehydrated DMF, and furfuryl alcohol (3.0 ml/34.6 mmol) was added to the solution. The reaction mixture was stirred for 12 h at 75 °C and then cooled down to room temperature. The macromonomer, PEA2F, was precipitated by excess methanol. The yield was 12.7 g (75%). PEA2F was used without further purification. GPC: $M_n=8700$, $M_w/M_n=1.58$. DSC: $T_g=-34$ °C and $T_m=54$ °C. IR (cm^{-1}): 3359, 2960, 2877, 1739, 1603, 1537, 1456, 1382, 1226, 1178 and 1084. ^{1}H NMR [DMSO-d_6, δ (ppm)]: 1.51 (s, 132H, –OCCH$_2$(CH$_2$)$_2$–), 2.08 (s, 6H, CH$_3$), 2.29 (s, 132H, –OCCH_2(CH$_2$)$_2$–), 4.14–4.24 (m, 136H, –OCH_2–), 5.06 (s, 4H, CH$_2$), 6.46 (s, 2H, CH), 6.53 (s, 2H, CH), 7.03–7.51 (m, 6H, aromatic), 7.68 (s, 2H, CH), 8.93 (s, 2H, NH), 9.65 (s, 2H, NH).

2.5. Polymerization of macromonomer with linkers by DA reaction

The macromonomer, PEA2F, and the linker, 3M (or 2M), (with furan/maleimide = 1/1) were dissolved in CHCl$_3$, and the solution was stirred at room temperature for 1 h. The solvent was then evaporated, and the reaction was proceeded at 60 °C for 15 h to obtain the adduct polymer, PEA2F3M or PEA2F2M.

In order to check the DA reactivity between PEA2F and 3M, the DA reaction in CDCl$_3$ solution was monitored by ^{1}H NMR spectroscopy. PEA2F and 3M (furan/maleimide = 1/1) were dissolved in CDCl$_3$ in a NMR test tube and kept at 60 °C. Then ^{1}H NMR spectra were measured at specified time intervals.

2.6. Recyclability of DA adduct polymers

Recyclability of the adduct polymers, PEA2F2M and PEA2F3M, was analyzed by applying multiple cycles of rDA and DA reactions to them. The rDA reaction was carried out as follows: DA adduct polymers were kept at 145 °C for 20 min and immediately dissolved in CHCl$_3$ at room temperature. The rDA products, which were fluid above T_m of PEA2F and soluble to CHCl$_3$, were analyzed by ^{1}H NMR and GPC. The DA reaction was carried out at 60 °C for 15 h. The DA products from PEA2F2M, which were soluble to CHCl$_3$, were analyzed by ^{1}H NMR and GPC. The DA products from PEA2F3M, which were elastic and became a gel in any solvent of PEA, were evaluated by tensile test. In PEA2F3M, crystallization gradually proceeded at room temperature. In order to exclude the influence of the degree of crystallinity from the result of the tensile test, the DA products were kept at room temperature for three weeks to reach the equilibrium crystallinity before the test.

3. Results and discussion

3.1. Model DA-rDA reaction of furan and maleimide groups

In order to investigate the thermal reversibility of the DA reaction between furan and maleimide groups, the reaction of furfuryl acetate and *N*-ethylmaleimide was examined under some conditions. Fig. 1 shows the ^{1}H NMR spectrum of the reaction product from equimolar amounts of furfuryl acetate and *N*-ethylmaleimide kept at 60 °C for 5 h. The product contains the *endo* adduct, the *exo* adduct and the unreacted starting compounds (Scheme 2). The peaks at 4.40–4.95 ppm are assigned to H8(*endo*) and H8(*exo*) protons of *endo* and *exo* adducts, (H8(*endo*): 4.56, 4.83 ppm, H8(*exo*): 4.41, 4.93 ppm) [9,17,23]. The peak at 5.02 ppm was assigned to H8$'$ of the unreacted furfuryl acetate. The contents of the *endo* adduct, the *exo* adduct and the unreacted furfuryl acetate was determined by the relative integrals of H8(*endo*), H8(*exo*) and H8$'$. Table 1 summarizes the mole fraction of them under various conditions. The yield of the DA adduct at 60 °C for 5 h was 95% (*endo*/*exo* = 64%/31%), while the yield was only 67% (*endo*/*exo* = 51%/16%) at room temperature. The equilibration of the DA reaction requires long time at room temperature, the yields of the DA adduct was increased to 95% (*endo*/*exo* = 73%/22%) when the reaction time was extended for 48 h. At 145 °C the yield of the DA adduct was decreased to 56% (*endo*/*exo* = 12%/44%). So, the retro reaction is preferred at higher temperatures. Though the ratio of *endo*/*exo* also changes depending on the temperature, this change is out of the scope of this study.

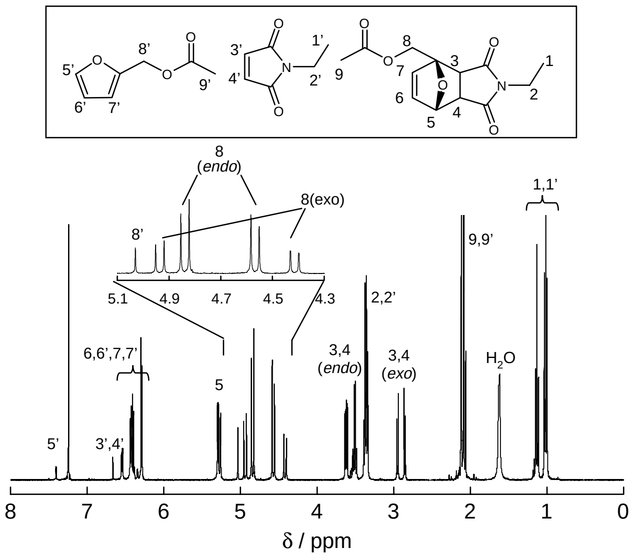
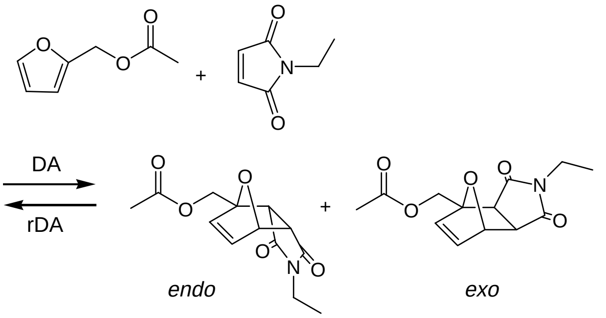


Fig. 1. ^{1}H NMR spectrum of the product of model DA reaction. The product contains *endo*, *exo* isomers and unreacted starting materials.



Scheme 2. Model Diels–Alder reaction.

3.2. Synthesis of macromonomer PEA2F

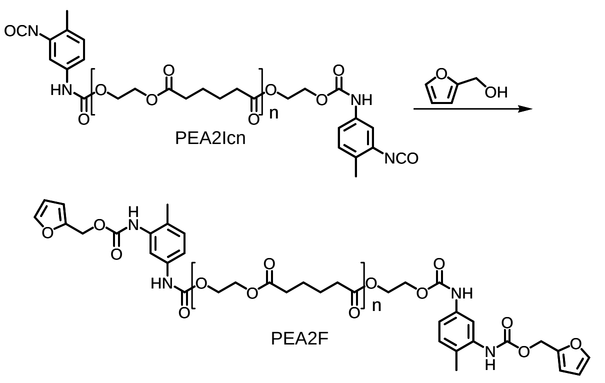
The macromonomer, PEA2F, was synthesized by condensation of PEA2Icn and furfuryl alcohol (Scheme 3). In the ^{1}H NMR spectrum of the reaction product, no peaks were ascribed to the unreacted furfuryl alcohol. The absorption from isocyanate groups, which is clearly found at 2277 cm^{-1} in the IR spectrum of PEA2Icn, disappeared in the spectrum of the product. Thus, all the isocyanate end groups of PEA2Icn were condensed with furfuryl alcohol to form furanic end groups. The molecular weight of this product, PEA2F, was estimated by GPC: M_n(GPC) = 8700, $M_w/M_n = 1.58$. The ^{1}H NMR data shows that PEA2F contains 6.1×10^{-2} mol of furanic groups per 1 mol of ethylene adipate. From this value, M_n(NMR) of the product is estimated to be 6300. Considering that M_n(GPC) represents the molecular weigh relative to polystyrene standards, the difference between M_n (NMR) and M_n (GPC) is within a reasonable error.

3.3. Copolymerization and depolymerization of PEA2F and 2M

Copolymerization of PEA2F and 2M (furan/maleimide = 1/1) by DA reaction was carried out at 60 °C for 15 h (Scheme 4). From the GPC analysis, M_n of the reaction product, PEA2F2M, is 18,300, which is about twice as large as that of the starting macromonomer, PEA2F ($M_n = 8700$). The polydispersity ($M_w/M_n = 2.43$) of PEA2F2M is also larger than that of PEA2F ($M_w/M_n = 1.58$). In the ^{1}H NMR spectrum of PEA2F2M, the peaks attributed to the DA adduct moiety were detected at 4.40–4.95 ppm, although large peaks from the unreacted furan groups at 5.11 ppm still remained. These data indicate that though the DA reaction certainly proceeds between the furan groups of PEA2F and the maleimide groups

Table 1
Yields of DA reactions from furfuryl acetate and *N*-ethylmaleimide

Temperature (°C)	Time (h)	*endo* (%)	*exo* (%)	Unreacted (%)
rt	5	51	16	33
rt	48	73	22	5
60	5	64	31	5
145	0.33	12	44	44

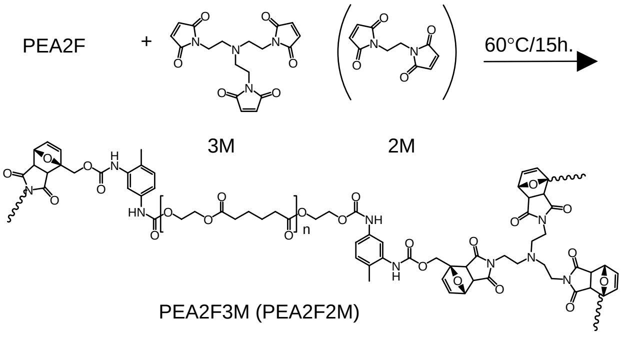


Scheme 3. Synthesis of PEA2F.

of 2M under this condition, the reactivity is not enough to achieve polymerization of PEA2F and 2M.

The reversibility of the DA reaction was examined for PEA2F2M. PEA2F2M was kept at 145 °C for 20 min to disconnect the DA adduct moiety by rDA reaction. After the reaction, the rDA product was immediately dissolved in $CHCl_3$ to avoid the re-progress of the forward DA reaction. The molecular weight and molecular weight distribution of the rDA product were $M_n = 8800$ and $M_w/M_n = 1.63$. Both of them were similar to the starting macromonomer, PEA2F. In the ^{1}H NMR spectrum of the rDA product, the peaks at 4.40–4.95 ppm, which are ascribed to the DA adduct moiety, were completely disappeared. These data indicate that the DA adduct moieties in PEA2F2M was completely disconnected to recover the starting PEA2F and 2M at 145 °C for 20 min. Note that in the DA reaction of the low molecular weight model discussed above, 56% of the DA adducts remains at the same temperature (Table 1). The higher yield of the rDA product in PEA2F2M probably comes from the difference in the reaction medium. In the PEA2F2M system, furan and maleimide groups generated by the rDA reaction can scarcely encounter again in the sea of PEA chains. This must depress the rate of the forward DA reaction.

The recyclability of PEA2F2M was investigated by applying cycles of DA (=polymerization) and rDA (=depolymerization) up to four times. The polymerization was done at 60 °C for 15 h and the depolymerization was done at 145 °C for 20 min. On each cycle, the molecular weight of the DA and rDA products was analyzed by GPC. The results are shown in Fig. 2. Up to four cycles, M_n of all the DA products are around 18,000, which is about twice as large as that of the macromonomer, PEA2F. The polydispersities of all the DA products are also larger than that of PEA2F. On the other hand, the molecular weight and polydispersity of the rDA product were similar to those of PEA2F. These data indicate that PEA2F2M is tolerant to the cycle of DA and rDA reactions up to at least four times.



Scheme 4. Copolymerization of PEA2F with 2M and 3M.

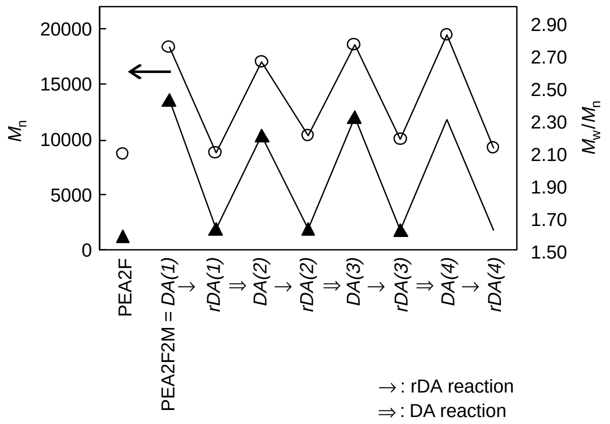


Fig. 2. Thermal recyclability of PEA2F2M. Number average molecular weight (○) and polydispersity (▲) of the DA and rDA products are shown. The DA reaction (indicated by ⇒) was done at 60 °C for 15 h. The rDA reaction (indicated by →) was done at 145 °C for 20 min.

3.4. Copolymerization of PEA2F and 3M by DA reaction

The DA reactivity between PEA2F and 3M (Scheme 4) was monitored in solution by ^{1}H NMR spectroscopy. PEA2F and 3M (furan/maleimide = 1/1) were dissolved in $CDCl_3$ in a NMR tube and it was kept at 60 °C. ^{1}H NMR spectra were measured at specified time intervals. Fig. 3(a) shows ^{1}H NMR spectrum before the DA reaction. No peaks corresponding to the DA adduct was observed between 4.40 and 4.95 ppm. After 5 h reaction at 60 °C, the spectrum has the peaks of the DA additive between 4.40 and 4.95 ppm (Fig. 3(b)). Thus, the DA reactivity between PEA2F and 3M was confirmed. After 15 h reaction, the sample became a gel and all the peaks in the ^{1}H NMR spectrum became broad (Fig. 3(c)). This result indicates the formation of a 3D-network structure.

Bulk copolymerization of PEA2F and 3M (furan/maleimide = 1/1) was carried out at 60 °C. The growth of the molecular weight of PEA2F3M was analyzed by GPC. Fig. 4 shows GPC traces of PEA2F3M obtained by the DA reaction for specified times. Within 8 h of reaction, the entire product was soluble to $CHCl_3$, while part of the product became insoluble by the reaction over 10 h. The content of the insoluble fraction increased with the reaction time. After the reaction for 15 h, only a few percent of the product was soluble to $CHCl_3$. The data of 10, 12 and 15 h in Fig. 4 shows the GPC curve of the soluble fractions. As the reaction time increased from 0 to 12 h, the GPC trace sifted to higher molecular weight range. The molecular weight distribution also became broader with the reaction time. After the reaction of 15 h, however, the molecular weight and

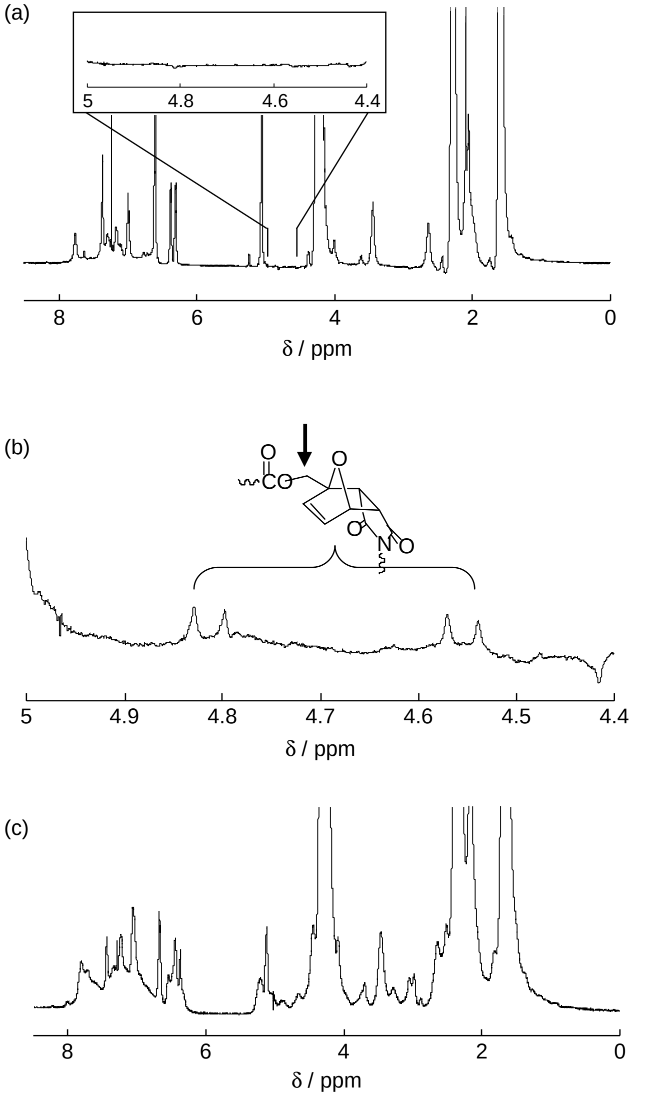


Fig. 3. ^{1}H NMR spectrum of the reaction mixture of PEA2F and 3M kept at 60 °C for (a) 0 h, (b) 5 h and (c) 15 h in $CDCl_3$. Inset in (a) shows the expansion of the spectrum (a).

molecular weight distribution of the soluble fraction became similar to the macromonomer, PEA2F. Since, the soluble fraction in the product was only a few percent after 15 h reaction, this fraction might consist of PEA without furanic terminal groups contained in the macromonomer as impurity. Thus, almost all the furanic terminated PEA was copolymerized by DA reaction to produce the 3D network structure.

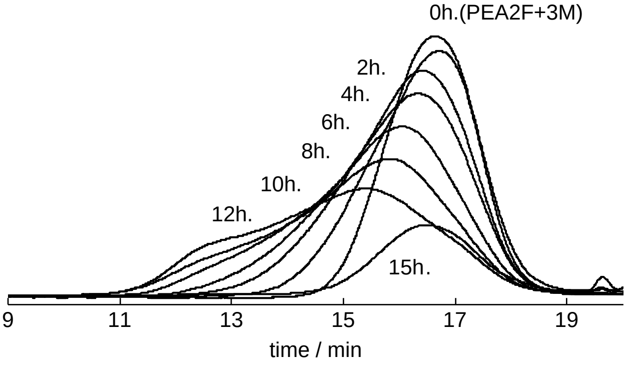


Fig. 4. GPC traces of PEA2F or PEA2F3M obtained at each DA reaction time. Only the fraction soluble to $CHCl_3$ was analyzed for the samples of 10–15 h.

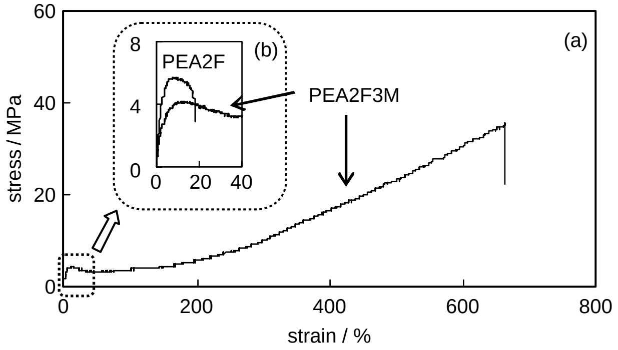


Fig. 5. Stress–strain curves of PEA2F3M (a) and PEA2F (b).

The GPC results indicate that the DA reaction at 60 °C for 15 h is enough for the copolymerization of PEA2F and 3M. Hereafter, we analyze the product obtained by the copolymerization of PEA2F and 3M (furan/maleimide = 1/1) at 60 °C for 15 h. The product, PEA2F3M, was insoluble to solvents of PEA, but formed a gel in $CHCl_3$. This indicates the formation of a 3D-network structure with ultra high molecular weight. The molecular weight of PEA2F3M is obviously much higher than that of PEA2F2M obtained by the same reaction condition. The difference in the number of reactive groups between 2M and 3M can be one of the factors that induce the difference in the molecular weight. 3M has three maleimide groups while 2M has two.

The gradual crystallization of PEA2F3M was observed at room temperature. Just after the DA reaction at 60 °C for 15 h, PEA2F3M as a plate was transparent while it gradually became opaque by crystallization after a week. This feature is different from that of PEA2F and PEA2F2M. PEA2F and PEA2F2M crystallizes in a minute at room temperature. DSC analysis shows that the melting point, T_m, of PEA2F3M is 47 °C, which is 7 °C lower than that of PEA2F. The glass transition temperature, T_g, of PEA2F3M is −34 °C, which is the same as that of PEA2F. The 3D-network structure and the T_g lower than room temperature result in the elasticity of PEA2F3M. Fig. 5 shows the stress–strain curve of PEA2F3M and PEA2F. PEA2F3M exhibits a stress–strain curve of a typical elastomer with low crystallinity, while PEA2F shows behavior of a weak brittle plastic. Tensile strength, elongation at break, and tensile modulus of PEA2F3M and PEA2F are plotted in Fig. 6. These values were averaged over the data of at least five samples.

3.5. Depolymerization of PEA2F3M by rDA reaction

Thermal property of PEA2F3M was analyzed by DSC. Fig. 7 shows the DSC thermograms of PEA2F3M just after the DA reaction. The sample was first heated from −50 to 200 °C (1st heating), followed by cooling to −50 °C (1st cooling) and reheating to 200 °C (2nd heating). The heating and cooling rates were kept at 20 °C/min throughout the DSC

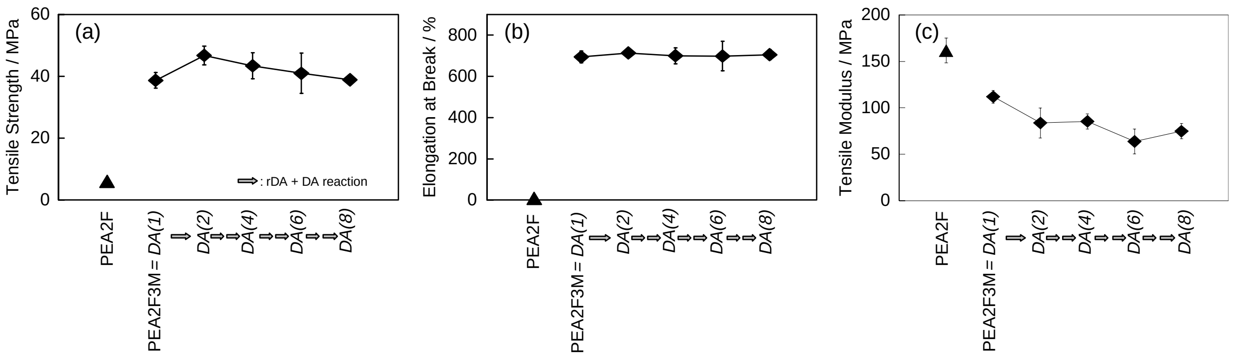


Fig. 6. (a) Tensile strength, (b) elongation at break, and (c) tensile modulus of PEA2F (▲) and PEA2F3M (◆). The data for recycled PEA2F3M are also shown. The DA reaction was done at 60 °C for 15 h. The rDA reaction was done at 145 °C for 20 min.

measurement. During the 1st heating, a broad endothermic peak was observed at ca. 130 °C, which is ascribed to the rDA reaction. In the following 1st cooling and 2nd hearting scans, no peaks were observed. This result suggests that the depolymerization of PEA2F3M by rDA reaction was completed during the 1st heating, and the repolymerization by DA reaction did not occur during the 1st cooling and 2nd heating. As mentioned above, copolymerization of PEA2F and 3M by DA reaction is a very slow process that takes 15 h. The thermal treatment during the DSC scan did not allow the repolymerization.

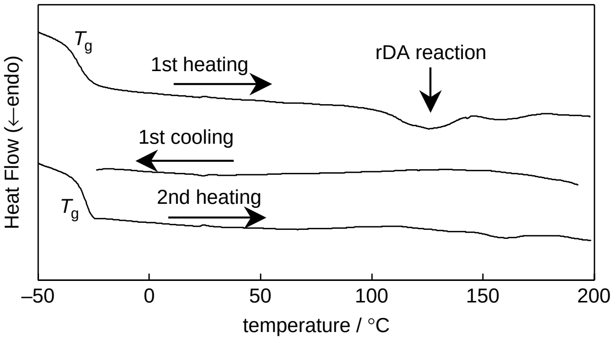


Fig. 7. DSC curves of PEA2F3M just after the DA reaction.

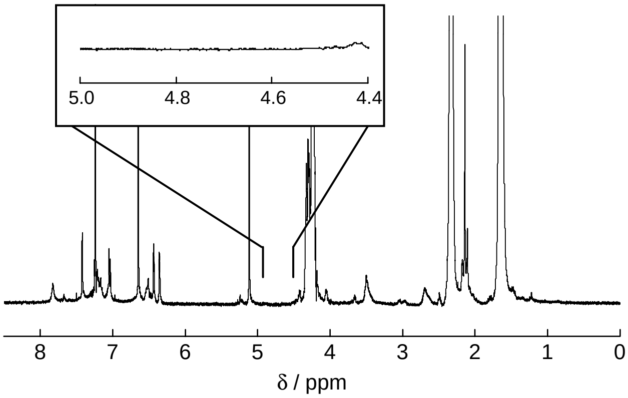


Fig. 8. ^{1}H NMR spectrum of the rDA product from PEA2F3M. Inset shows the expansion of the spectrum.

PEA2F3M was depolymerized by rDA reaction at 145 °C for 20 min. Different from the starting PEA2F3M, the rDA product was fluid above T_m (=54 °C) of PEA2F and soluble to $CHCl_3$. This behavior indicates that the 3D-network of PEA2F3M was disconnected by rDA reaction to reproduce PEA2F and 3M. Fig. 8 shows the ^{1}H NMR spectrum of the rDA product. No peaks in this spectrum are ascribed to the DA adduct moieties. Only the peaks of PEA2F and 3M are detected. Molecular weight of the rDA product (M_n=10,000, M_w/M_n=1.68) is similar to that of PEA2F (M_n=8700, M_w/M_n=1.58). These results suggest that PEA2F3M was completely depolymerized to reproduce PEA2F by rDA reaction at 145 °C for 20 min.

3.6. Recyclability of PEA2F3M

The recyclability of PEA2F3M was tested by applying a series of thermal cycles that consisted of the copolymerization by DA reaction at 60 °C for 15 h and the depolymerization by rDA reaction at 145 °C for 20 min. The cycles of DA and rDA reactions was repeated up to eight times. The rDA products were analyzed by GPC. Fig. 9 shows the number average molecular weight, M_n, and polydispersity, M_w/M_n, of the rDA products. Though M_n of the rDA product was kept constant, M_w and polydispersity gradually increases by the repetition of the DA and rDA reactions. This indicates that the molecular weight distribution of the rDA products became broader to the

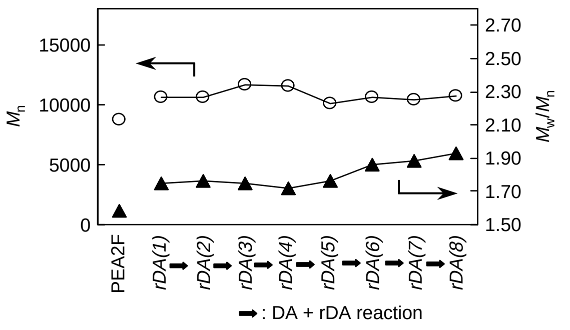


Fig. 9. Thermal recyclability of PEA2F3M. Number average molecular weight (○) and polydispersity (▲) of the rDA products. The DA reaction was done at 60 °C for 15 h. The rDA reaction was done at 145 °C for 20 min.

direction of the larger molecular weight. The mechanical properties of the recycled PEA2F3M films were evaluated by tensile test. The results are plotted in Fig. 6. Though the tensile modulus of PEA2F3M tended to decrease a little by the repetition of the cycles, the tensile strength and elongation at break of the recycled PEA2F3M were kept the values similar to the first DA product. Since, the elastic behavior rather than plasticity characterizes PEA2F3M, the decrease in the tensile modulus is not a severe problem. Thus, we have confirmed that PEA2F3M can be recycled at least eight times.

4. Conclusion

In this study, we have designed and synthesized polymers that can repeatedly polymerize and depolymerize at moderate conditions by DA/rDA reaction. A macromonomer, PEA2F, was prepared and copolymerized with multi-maleimides, 2M and 3M, by DA reaction at 60 °C. The reaction with 2M proceeded partially to give a polymer, PEA2F2M, whose molecular weight was only twice as large as PEA2F. The depolymerization of PEA2F2M, on the other hand, proceeded completely at 145 °C to reproduce the macromonomer, PEA2F. The cycles of DA and rDA reactions could be repeated up to four times without the decomposition of PEA2F. So, the recyclability of this polymer system was confirmed. The copolymerization of PEA2F and 3M gives a 3D network polymer, PEA2F3M. PEA2F3M shows elasticity at room temperature. The recyclability of this polymer was also confirmed up to eight times. The cycles of DA and rDA reactions induced neither loss of elasticity of the DA products nor reduction of the molecular weight of the rDA product. Thus, we have successfully obtained readily recyclable polymers.

PEA2F2M and PEA2F3M are made from a macromonomer having two furanic groups at both chain ends and multi-maleimides. By simply replacing the main component of the macromonomer, we can freely design the properties of polymeric materials with recyclability.

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