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Poly(olefin sulfone)s

Takeo Sasaki, Khoa Van Le and Yumiko Naka

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Abstract

In this chapter, we introduce poly(olefin sulfone)s and review the recent progress on the photoinduced depolymerization of poly(olefin sulfone)s as well as their applications. Poly(olefin sulfone)s combined with photobase generators (PBGs) are depolymerized upon irradiation with light. A poly(olefin sulfone) is a 1:1 alternating copolymer of olefin monomer and sulfur dioxide in which the protons on the carbons adjacent to the sulfonyl groups can be readily abstracted by a base. This removal leads to a depolymerization chain reaction, resulting in incorporation of a photobase generating chromophore that can undergo a photoinduced unzipping reaction. During this reaction, the original olefin monomer and sulfur dioxide are regenerated from the primary chain of the poly(olefin sulfone). The photoinduced depolymerization of poly(olefin sulfone)s has been investigated for a wide variety of applications, including stereolithography, printable microcircuit fabrication, and removable adhesives.

Keywords: poly(olefin sulfone)s, depolymerization, photopolymers, dismantlable adhesives

1. Introduction

Photopolymers can change their physical and/or chemical properties through the absorption of light [1]. Although many studies on photopolymers have been reported, a few studies show photoinduced conversion to monomers under mild conditions. If a portion of the polymer is converted completely into monomers under light irradiation, the average molecular weight decreases, and this process has potential application to sophisticated device processing, including stereolithography without solvents. Such depolymerization under mild conditions is expected to yield recyclable (and, thus, environmentally friendly or “green”) polymers. However, most of the depolymerizable polymers reported require X-ray or electron-beam irradiation to trigger the depolymerization process [2, 3]. Only a few reports describe use

of low-energy irradiation for the depolymerization [4–10]. The unzipping degradation of a polymer main chain containing heteroatoms by X-ray or electron-beam irradiation has been achieved. For a poly(1-butene sulfone), only partial depolymerization occurs, and olefins are present in the gas produced by the irradiation [11, 12].

Degradation of a poly(olefin sulfone) doped with a photosensitizer has been investigated [13]. The degradation of poly(1-butene sulfone) doped with pyridine N-oxide was induced by irradiation with 300-nm light. In this system, however, a crosslinking reaction occurs in addition to degradation of the main chain. The number of photoinduced breaks in the main chain was 10–12. High-efficiency depolymerization to constituent monomers was achieved for poly(olefin sulfone)s containing photobase generators using low-energy light irradiation.

2. Poly(olefin sulfone)s

Poly(olefin sulfone)s are copolymers of olefin monomers and sulfur dioxide (**Figure 1**). They possess sulfonyl groups ($-\text{SO}_2-$) in the main chain and are easily synthesized by radical polymerization of an olefin monomer in a liquefied sulfur dioxide [14]. Peroxides, such as tert-butyl hydroperoxide, benzoyl peroxide, and diethyl ether peroxides, are used as polymerization initiators. The peroxide and sulfur dioxide act as a redox initiator and generate a radical species that reacts with an olefin monomer (**Figure 2**). While the sulfonyl radical is fairly stable, the olefin radical is unstable. The olefin radical generated in liquefied sulfur dioxide immediately reacts with a sulfur dioxide molecule to form an alkylated sulfonyl radical. The sulfonyl radicals then react with the olefin monomers to generate a polymer chain. Note that the sulfur atom of the sulfonyl radical is positively charged; therefore, it cannot react with the sulfur atom of sulfur dioxide, which is also positively charged. In addition, the olefin monomer and sulfur dioxide form a 1:1 charge-transfer complex in the liquefied SO_2 solution. The olefin- SO_2 complex reacts like a monomer unit in the radical polymerization process. Thus, the resulting poly(olefin sulfone) is a 1:1 alternating copolymer of olefin monomers and SO_2 [15].

2.1. Synthesis of poly(olefin sulfone)s

At ambient pressure, sulfur dioxide gas liquefies when cooled to temperatures below -10.2°C . The polarity of liquefied sulfur dioxide is comparable to that of dichloromethane, so liquefied sulfur dioxide dissolves a wide range of olefins. A high-pressure polymerization tube containing 1.0 g of an olefin monomer and 3.2×10^{-4} mol of t-butyl hydroperoxide (a redox initiator) was connected to a vacuum line and cooled in liquefied nitrogen. The tube was evacuated, and 6.0 g of sulfur dioxide was added by transfer through a vacuum line. The mixture was stirred for 24 h at -13°C . The resulting polymer was reprecipitated in methanol. Examples of chemical structures of simple poly(olefin sulfone)s are shown in **Figure 3**.

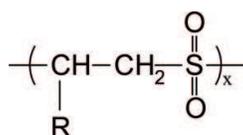


Figure 1. Structure of poly(olefin sulfone)s.

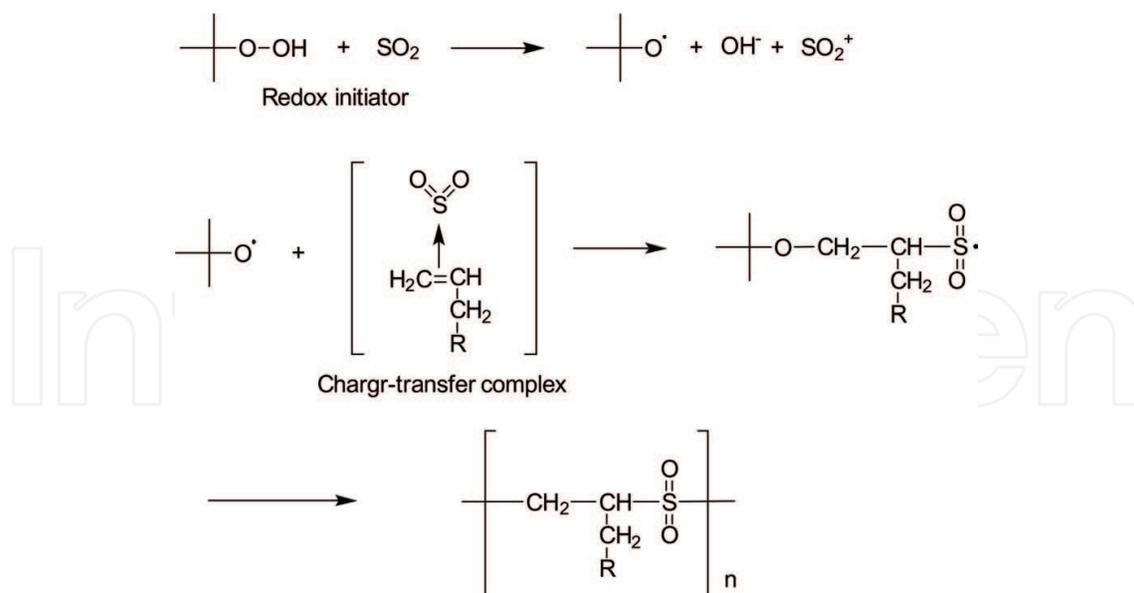


Figure 2. Polymerization of olefin monomers in liquefied sulfur dioxide.

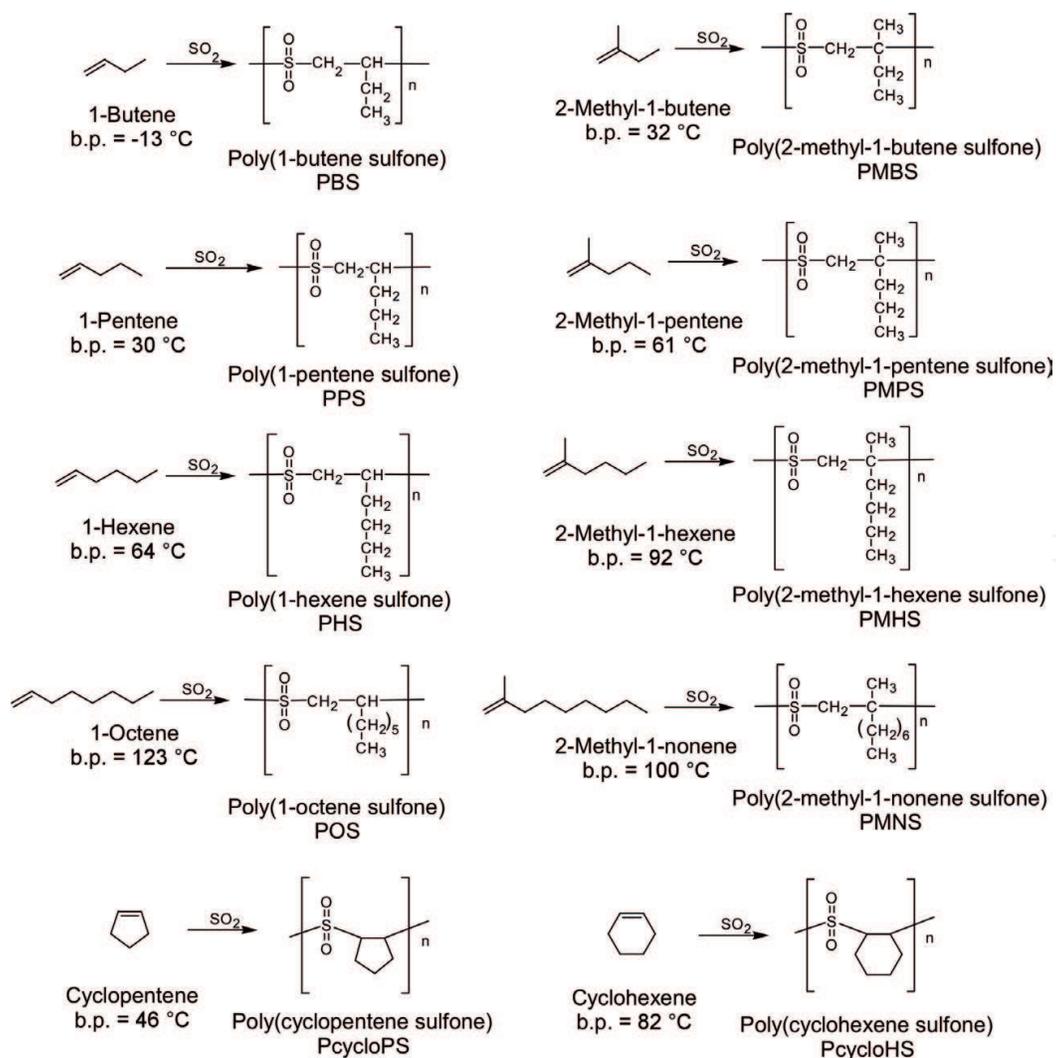


Figure 3. Examples of poly(olefin sulfone)s.

3. Depolymerization of poly(olefin sulfone)s

A sulfonyl group is a strong electron-withdrawing moiety. The electrons on the carbon atoms adjacent to the SO_2 groups are attracted by SO_2 , and thus, the protons on those carbons are easily removed by base [16]. When a proton on one of these carbons is removed, a chain reaction in which the main chain is depolymerized to the olefin monomer and sulfur dioxide occurs (Figure 4). Based on this process, the main chain of the poly(olefin sulfone) decomposes when mixed with bases such as piperidine, methylamine, or triethylamine. One example of base-induced depolymerization of poly(olefin sulfone)s is reaction of poly(N, N-diethyl 3-butenic amide sulfone) (DEBA) with 4,4'-trimethylenedipiperidine (base). The ^1H NMR spectrum of DEBA before addition of the base is shown in Figure 5(a). The change in the ^1H NMR spectrum after addition of the base

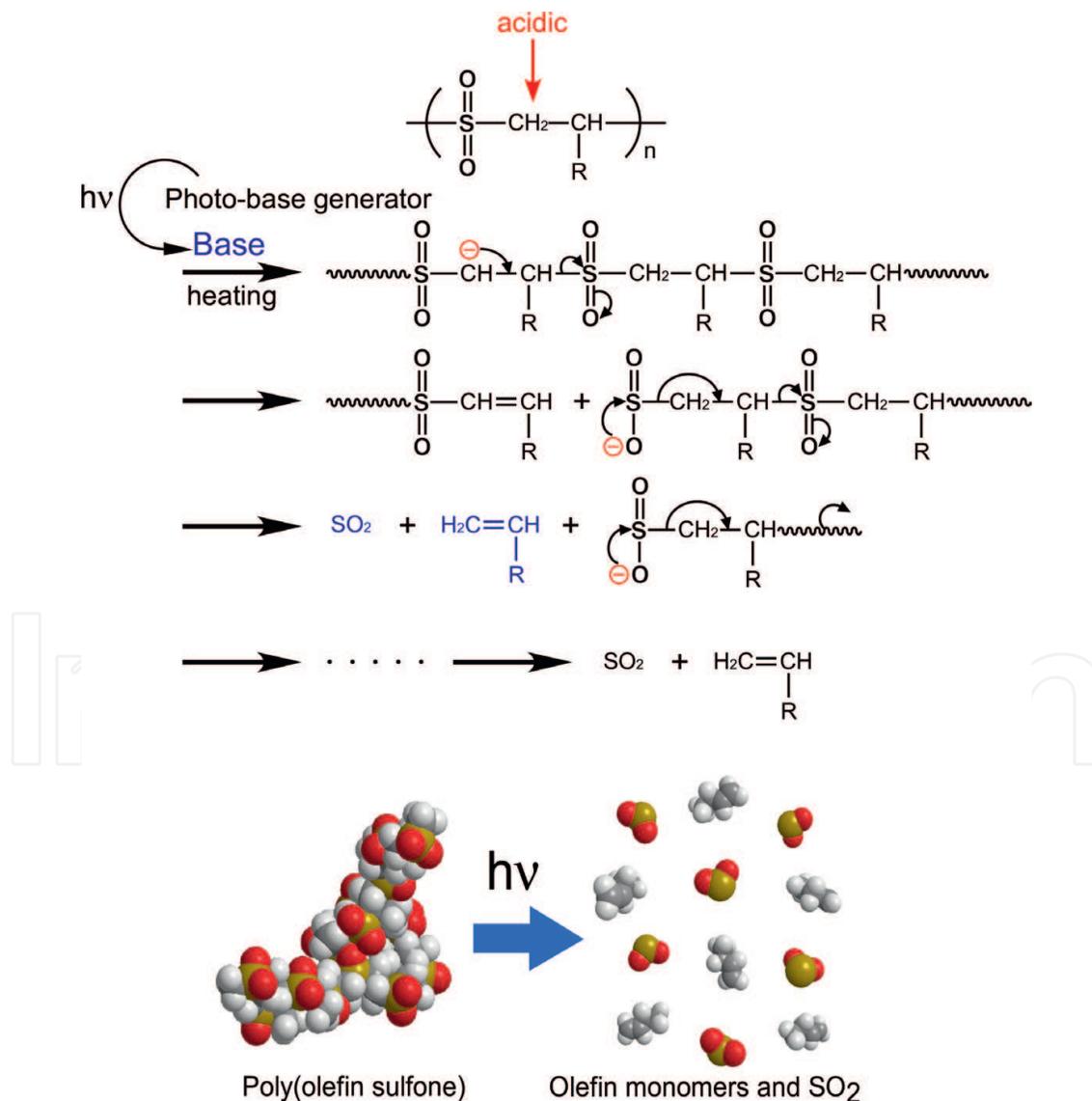


Figure 4. Photoinduced depolymerization of 1:1 alternating poly(olefin sulfone)s containing photo-base generating groups in the side chain.

is shown in **Figure 5(b)**. Signals of the olefin protons are easily recognized. In contrast, no change was observed in the DEBA solution without the addition of base, indicating that the decomposition of DEBA was caused by the added base. The ^1H NMR spectrum of the olefin monomer (N, N-diethyl 3-butenoic amide) is shown in **Figure 5(c)**. A comparison of **Figure 5(b)** and (c) showed that the major product in the resulting solution can be attributed

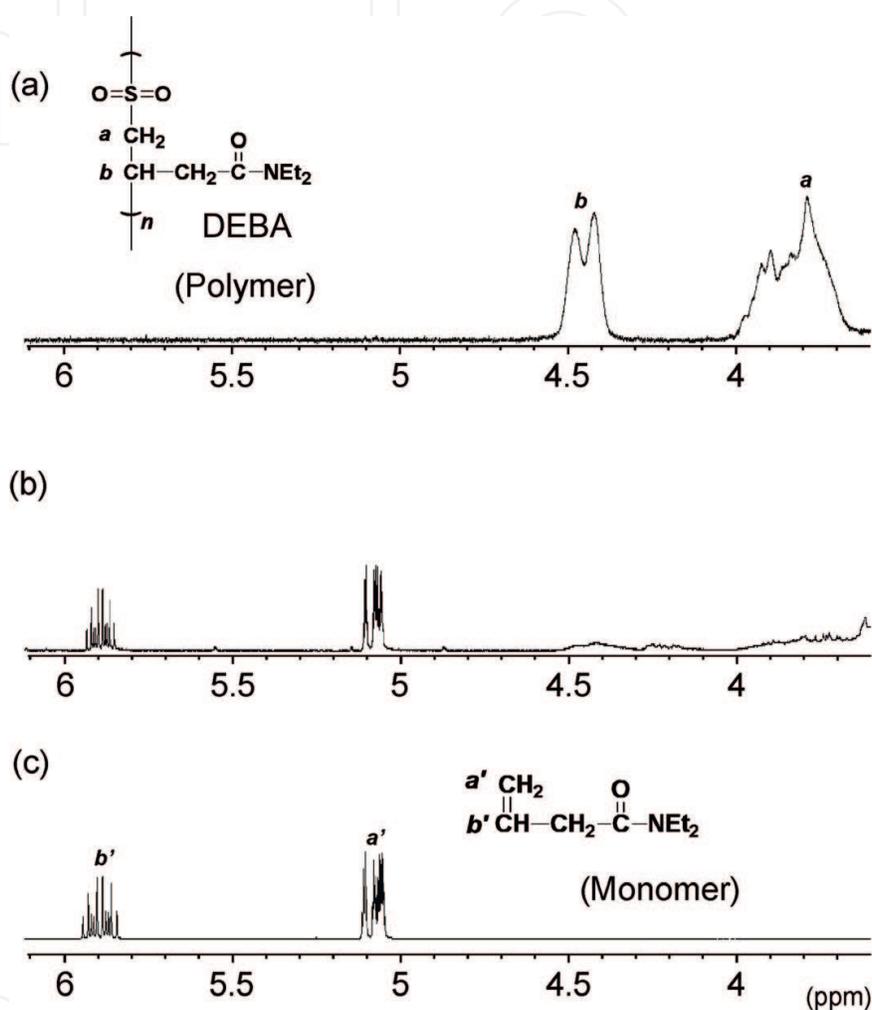


Figure 5. ^1H NMR spectra of DMSO-*d*₆ solutions of (a) DEBA, (b) DEBA mixed with 6.15 mmol/L 4,4'-trimethylenedipiperidine followed by heating at 100°C for 30 min, and (c) a monomer of DEBA.

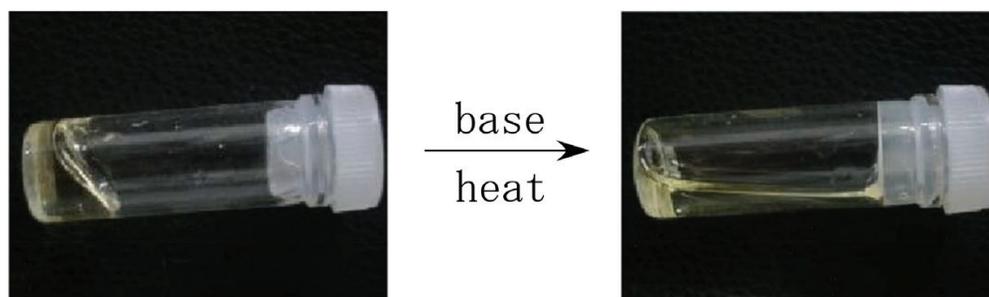


Figure 6. Photographs of the conc. solution of poly(olefin sulfone)s. The viscosity of the solution decreased rapidly when a trace of triethylamine was added to the solution.

to the DEBA monomer. **Figure 6** shows a picture of a concentrated solution of a poly(olefin sulfone). Although the viscosity of the solution was very high, when a trace of triethylamine vapor was added to the solution, the viscosity decreased immediately.

4. Photoinduced depolymerization of poly(olefin sulfone)s

A poly(olefin sulfone) possessing a photobase generating group depolymerizes upon photoirradiation and heating (**Figure 7**). Poly(olefin sulfone)s that possess photobase-generating groups were synthesized (**Figures 8 and 9**) [17]. The photobase-generating groups produce amine groups when irradiated with light. Photoinduced decomposition of the poly(olefin sulfone) was investigated using ^1H NMR. A poly(olefin sulfone) film was subjected to irradiation with 254-nm light, after which ^1H NMR spectra were recorded. **Figure 10(a)** and **(b)** show the ^1H NMR spectra of polymer 10 before and after irradiation, respectively, followed by heating. The progress of depolymerization was readily confirmed by the disappearance of the methylene and methine protons in the main chain (4.3–3.8 ppm), along with the appearance of signals near 5.1 and 5.8 ppm, which were assigned to protons on a vinyl group. The decomposition ratio of polymer 10 irradiated and heated under the conditions described above was estimated to be 95%. The decomposition ratio increased with the irradiation energy density (**Figure 11**). Conversion of the polymer to the olefin monomer (depolymerization ratio) was also estimated to be 50%. The irradiated film (polymer 10) after heating was dissolved in THF and the molecular weight measured by gel permeation chromatography (GPC) (**Figure 12**). The polymer completely disappeared and low-molecular-weight species appeared. The retention time of the lowest molecular weight species was coincident with that of the olefin monomer. The number average molecular weight decreased from 130,000 to 300.

As shown in **Figure 13**, a lithographic image with clear positive tone of alternating 40- μm wide lines and gaps on a film of polymer 10 could be developed with 0.012 M aq. HCl.

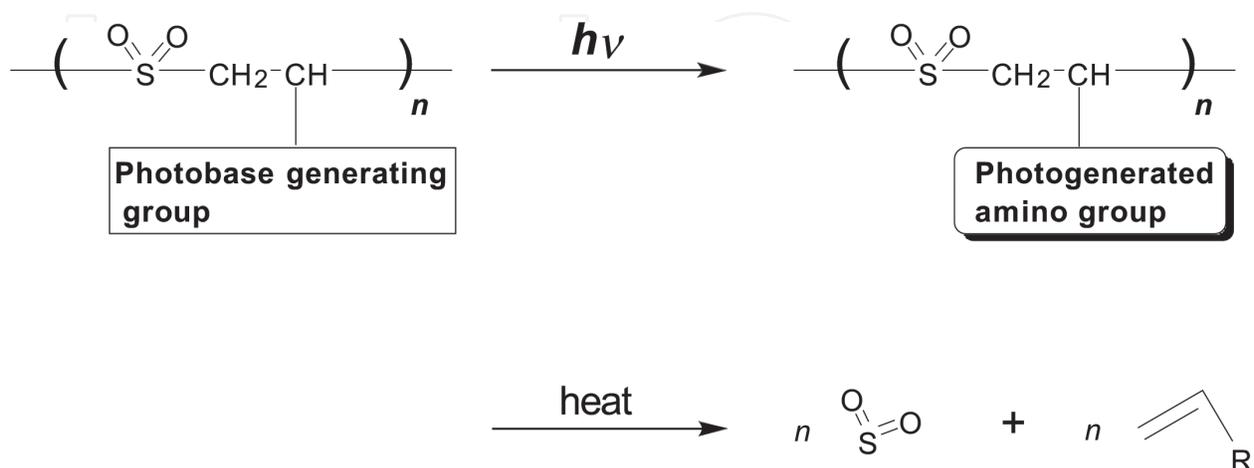


Figure 7. Proposed mechanism of base-catalyzed thermal depolymerization of 1:1 alternating poly(olefin sulfone)s.

Irradiation with 254-nm light triggered the generation of a base along with creation of a latent image. The visible image could be developed after heating the exposed polymer film.

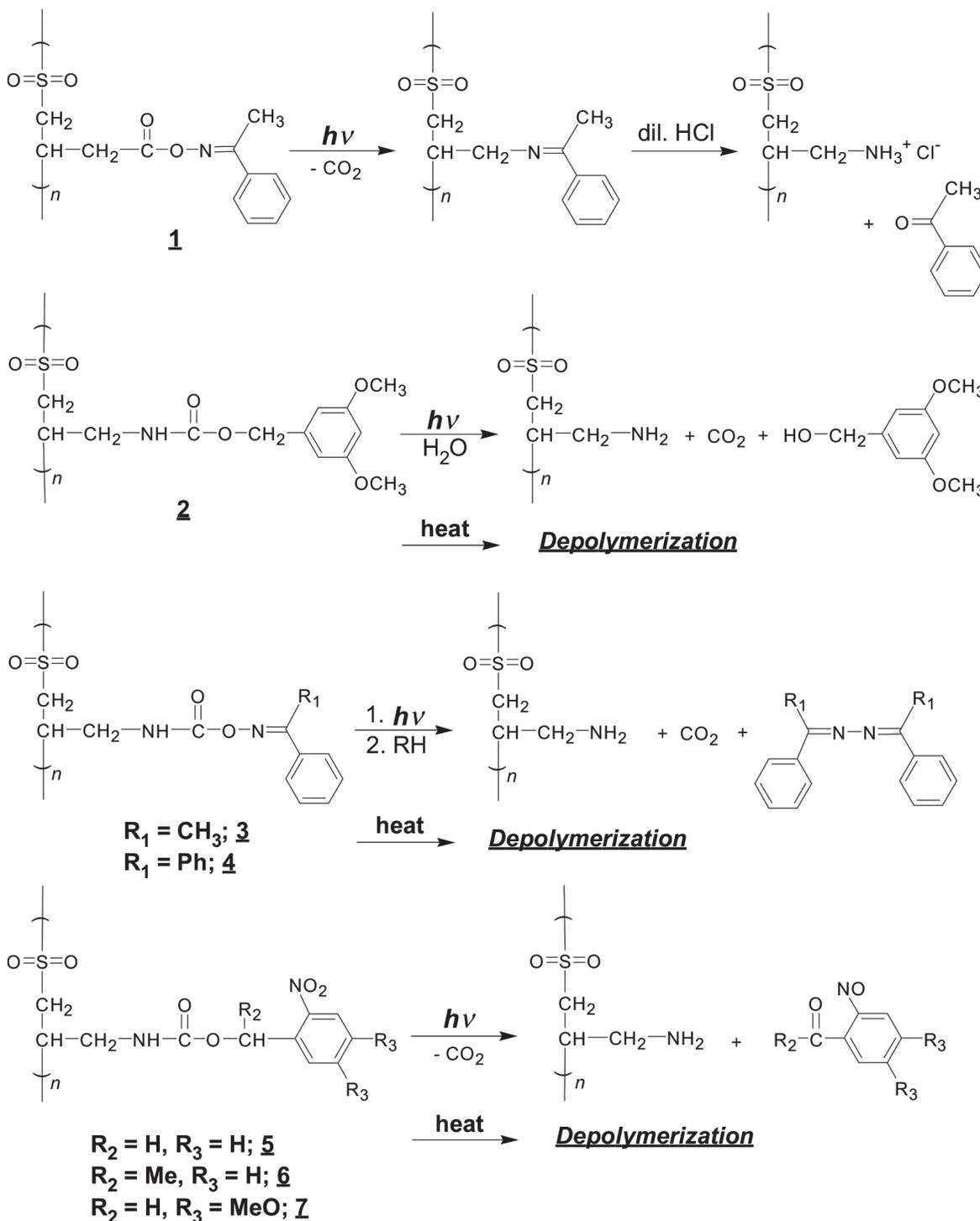


Figure 8. Structures of poly(olefin sulfone)s that generates primary amine by photo irradiation and the photochemical reactions of the pendant group.

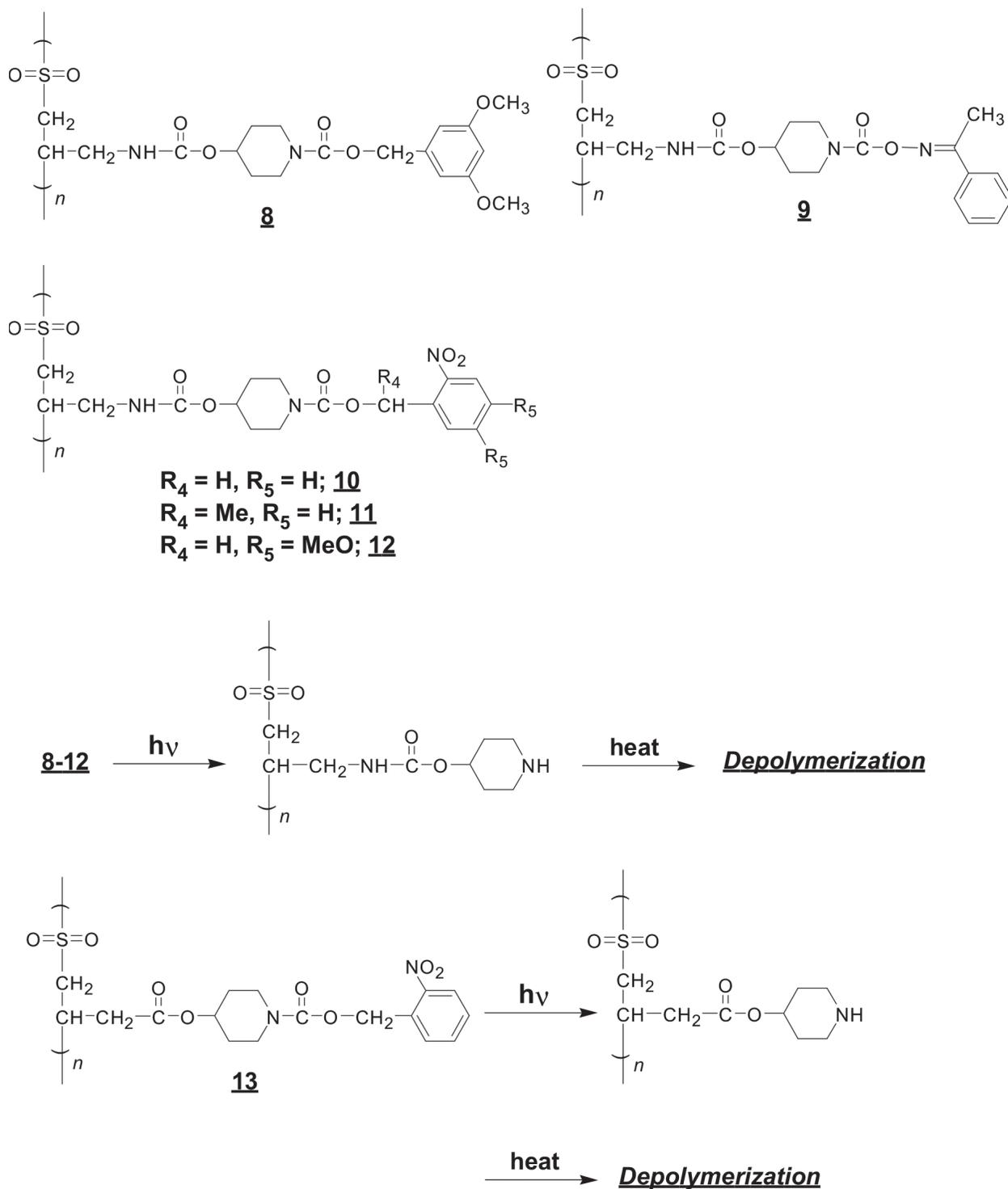


Figure 9. Structures of poly(olefin sulfone)s that generates secondary amine by photo irradiation and the photochemical reactions of the pendant group.

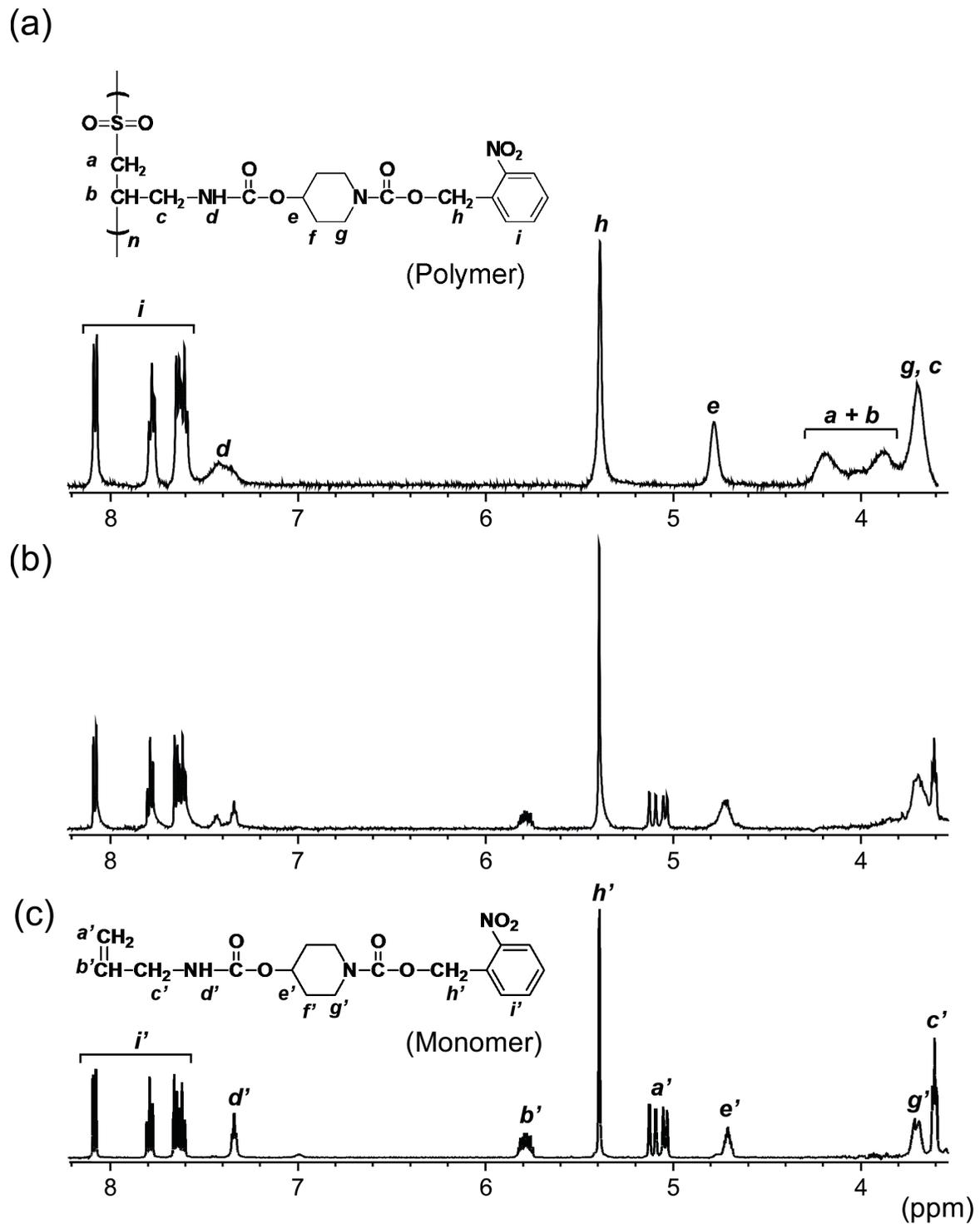


Figure 10. ^1H NMR spectra of polymer 10 in DMSO-d_6 (a) before UV irradiation, (b) after 254-nm irradiation of 600 mJ/cm^2 followed by heating at 150°C for 15 min, and (c) monomer 10.

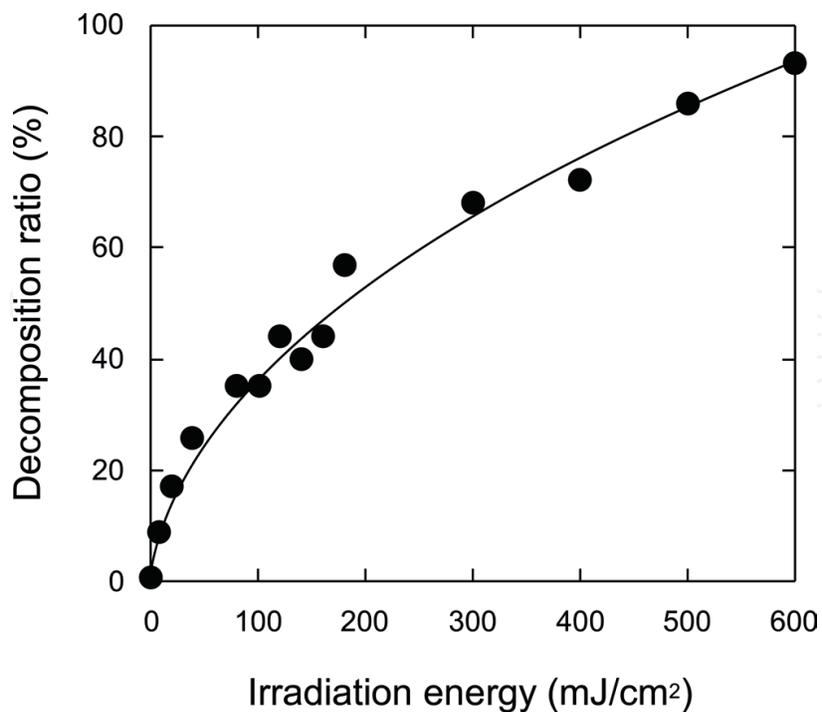


Figure 11. Decomposition ratio of polymer 10 heated at 150°C for 15 min after UV irradiation as a function of irradiation energy.

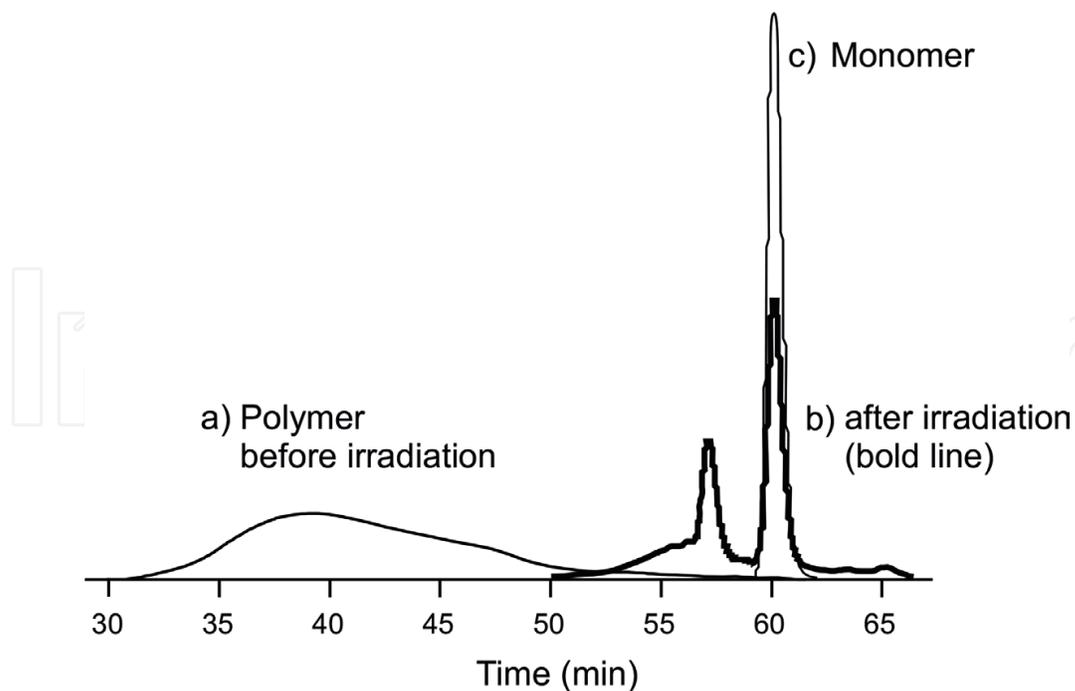


Figure 12. GPC curves of polymer 10 (a) before UV irradiation, (b) after UV irradiation at 600 mJ/cm², followed by heating at 150°C for 15 min, and (c) the corresponding olefin monomer.

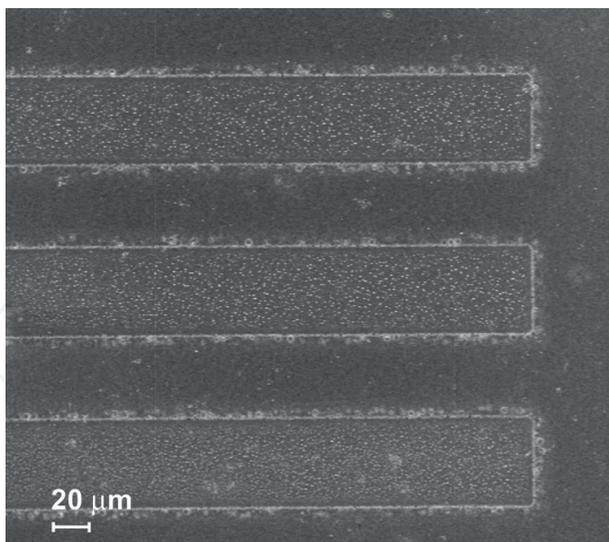


Figure 13. SEM image of polymer 10 film after UV irradiation at 100 mJ/cm², followed by heating at 130°C for 60 sec and washed with 0.012 M HCl(aq).

5. Effect of main chain structure on depolymerization of poly(olefin sulfone)s

Photoinduced depolymerization of the polymers shown in **Figure 3** mixed with a low-molecular-weight photo-base generator (ANC2) was investigated [18]. **Figure 14(a)** shows the change in the IR spectrum of PMPS film coated on a KBr plate without light irradiation, and **Figure 14(b)** shows the corresponding spectrum after light irradiation during heating (post-exposure heat treatment). The absorption spectrum of the nonirradiated film was independent of the heating time, whereas the sulfonyl stretching bands (1311 and 1130 cm⁻¹) decreased with the heating time after film irradiation, which indicates decomposition of the polymer main chain. The extent of decomposition increased with the irradiation energy density (**Figure 14(c)**), and the extent of PMPS decomposition was estimated to be 95%. Conversion of the polymer to the olefin monomer (extent of depolymerization) was estimated by ¹H NMR as 92%. Therefore, the polymer was converted to monomers with very high efficiency. **Figure 15(a)** shows the residual ratio of the PBS sulfonyl group as a function of heating time after photoirradiation. The change in residual ratio (decomposition of the main-chain) was slow compared to that for PMPS. In contrast, the change in the residual ratio of PMBS was as fast as that for PMPS (**Figure 15(b)**). The only structural difference between PBS and PMBS is the number of substituents on the main chain. Thus, the decomposition characteristics must be dependent on the structure of the main chain. **Figure 16** shows the residual ratios for all polymers as a function of heating time after photoirradiation. The results show that the decomposition characteristics of the polymers can be divided into two groups: poly(olefin sulfone)s that possess only one type of proton on the main chain (branched 1-olefins such as PMBS, PMPS, PMHS, and PMNS), and poly(olefin sulfone)s that possess two types of protons

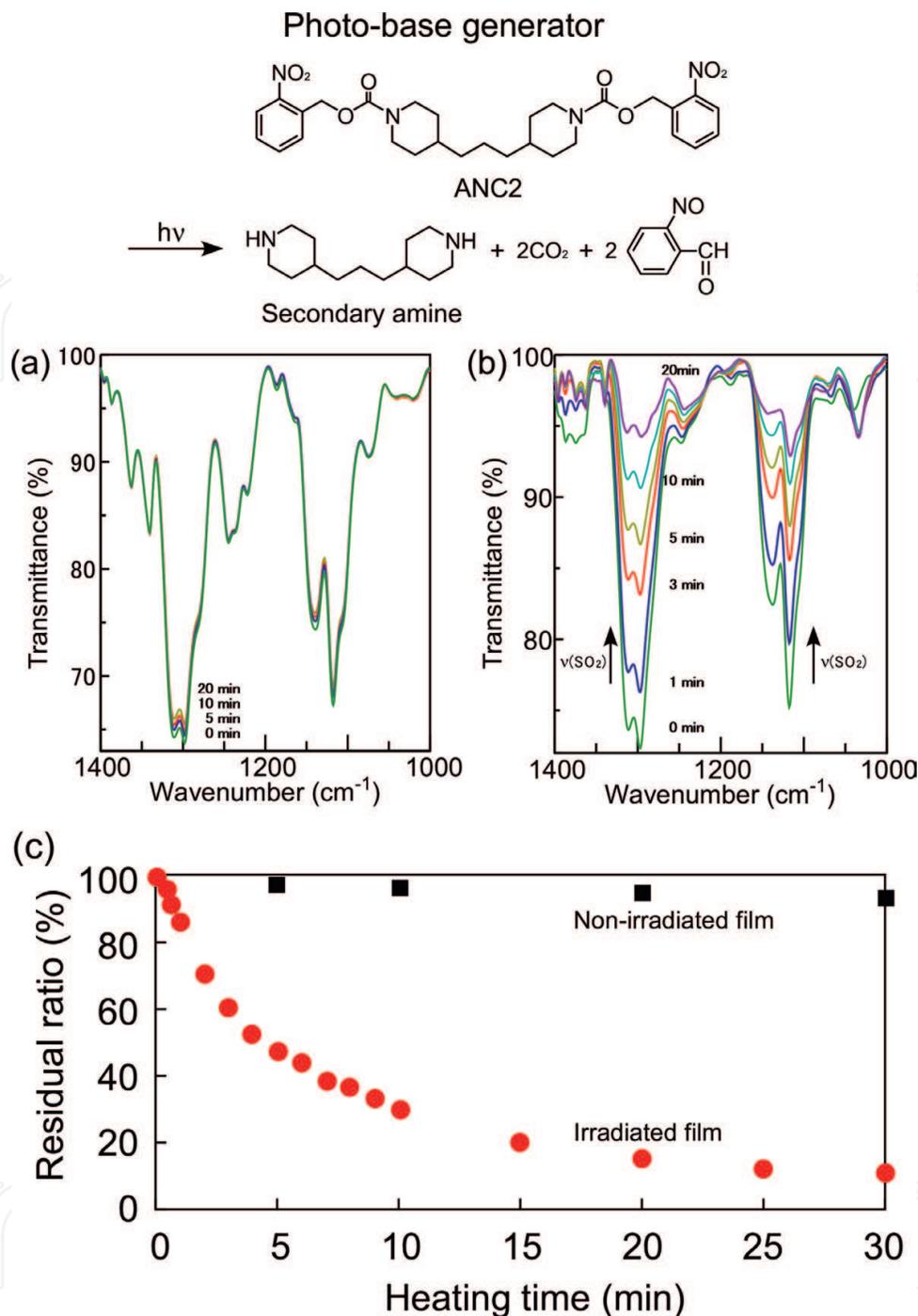


Figure 14. Changes in the IR absorption spectra of the sulfonyl group in PMPS coated on a KBr plate (a) without irradiation and (b) after light irradiation at 254-nm and 180 mJ/cm^2 . The thickness of the film was 2 μm . The post-exposure heat treatment time was varied from 0–15 min at 150°C. (c) Residual ratio of the PMPS main-chain as a function of heating time after irradiation, as estimated by IR absorption. The concentration of the L-ANC2 (photo-base generator) was 30 wt%. The heating temperature was 120°C and the irradiation energy was 3.15 J/cm^2 .

on the main chain (straight chain 1-olefins and cycloolefins such as PBS, PPS, PHS, PcycloPS, and PcycloHS). The poly(olefin sulfone)s possessing only one type of proton on the main chain can undergo extensive decomposition, whereas the poly(olefin sulfone)s possessing

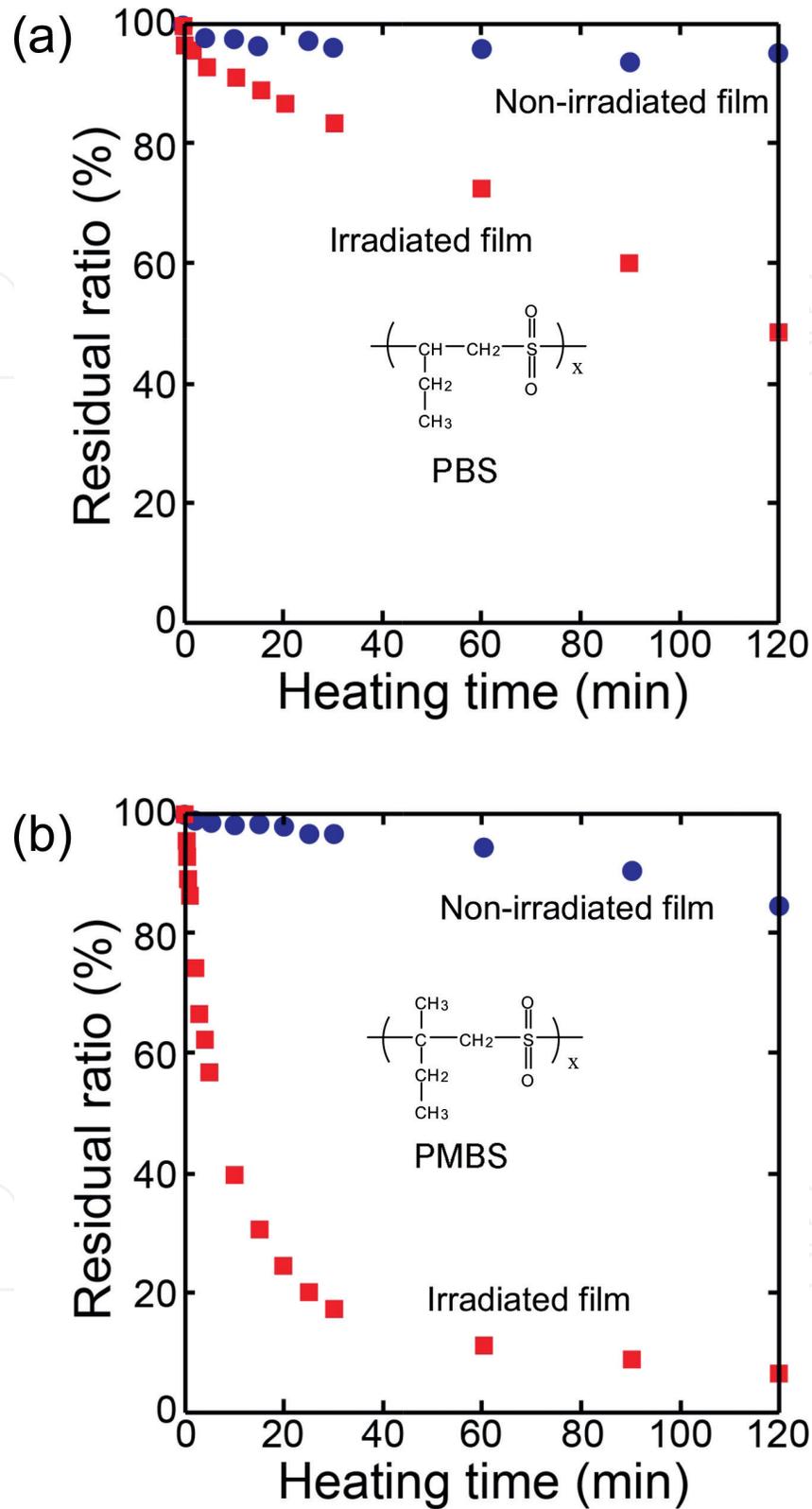


Figure 15. Residual ratios of the main-chain of poly(olefin sulfone)s in films estimated by IR absorption as a function of heating time after irradiation. (a) PBS film without irradiation (●) and after irradiation (■). (b) PMBS film without irradiation (●) and after irradiation (■). The concentration of the PBG was 30 wt%. The heating temperature was 120°C and the irradiation energy was 3.15 J/cm².

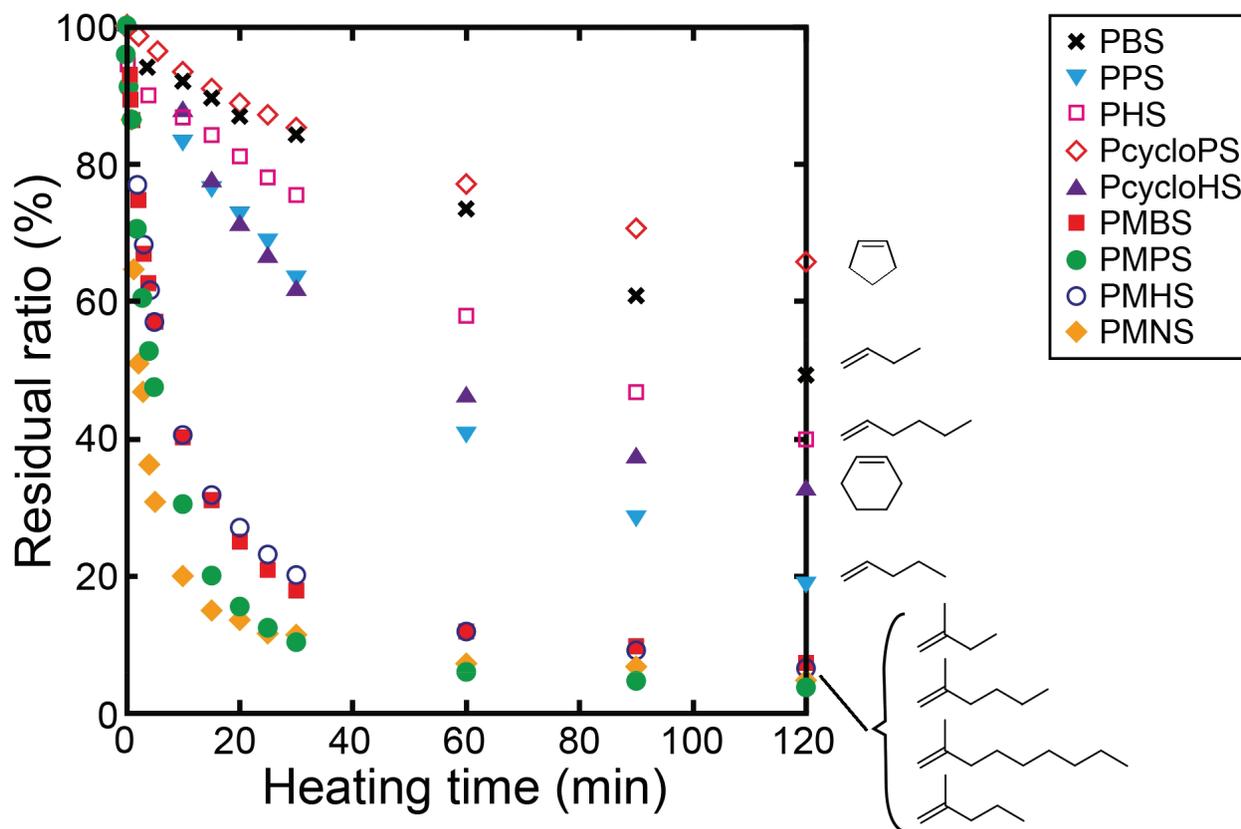


Figure 16. Residual ratios of the main-chains of poly(olefin sulfone)s in films as a function of heating time after irradiation. The concentration of the PBG was 30 wt%. The heating temperature was 120°C and the irradiation energy was 3.15 J/cm².

two types of protons on the main chain undergo only a low extent of decomposition. The number of protons that can be abstracted appears to affect the extent of depolymerization. When many protons existing on a single main chain are abstracted, the yield of monomers was reduced, as shown in the reaction mechanism in **Figure 4**.

6. Poly(olefin sulfone)s possessing a photobase generator and base amplifier

Photoinduced depolymerization of poly(olefin sulfone)s possessing a base-amplifying moiety in the side chain has been investigated using a film doped with a photobase-generating compound [19]. Poly(olefin sulfone)s that possess the 9-fluorenylmethoxycarbonyl (Fmoc) group as a base-labile N-protecting group have been synthesized (**Figure 17**). The Fmoc group can undergo amine-catalyzed thermolysis to an amino group with the evolution of carbon dioxide and dibenzofulvene [20, 21]. Therefore, the number of amino groups increased in the irradiated poly(olefin sulfone) films containing the Fmoc group and doped with PBGs during the subsequent heating step. Even though the irradiation produced few amino groups, their concentration could be amplified by the amine-catalyzed thermal degradation of the Fmoc group.

Figure 18 shows the decomposition ratio of P4 and P5 plotted as a function of irradiation energy density. The decomposition ratio of copolymer P4 was greater than that of P5. For P4, a decomposition ratio of 98% was obtained at an energy density of 900 mJ/cm². Thus, the presence of a base-amplifying group in the side-chain enhanced the amount of base generated in the P4 film.

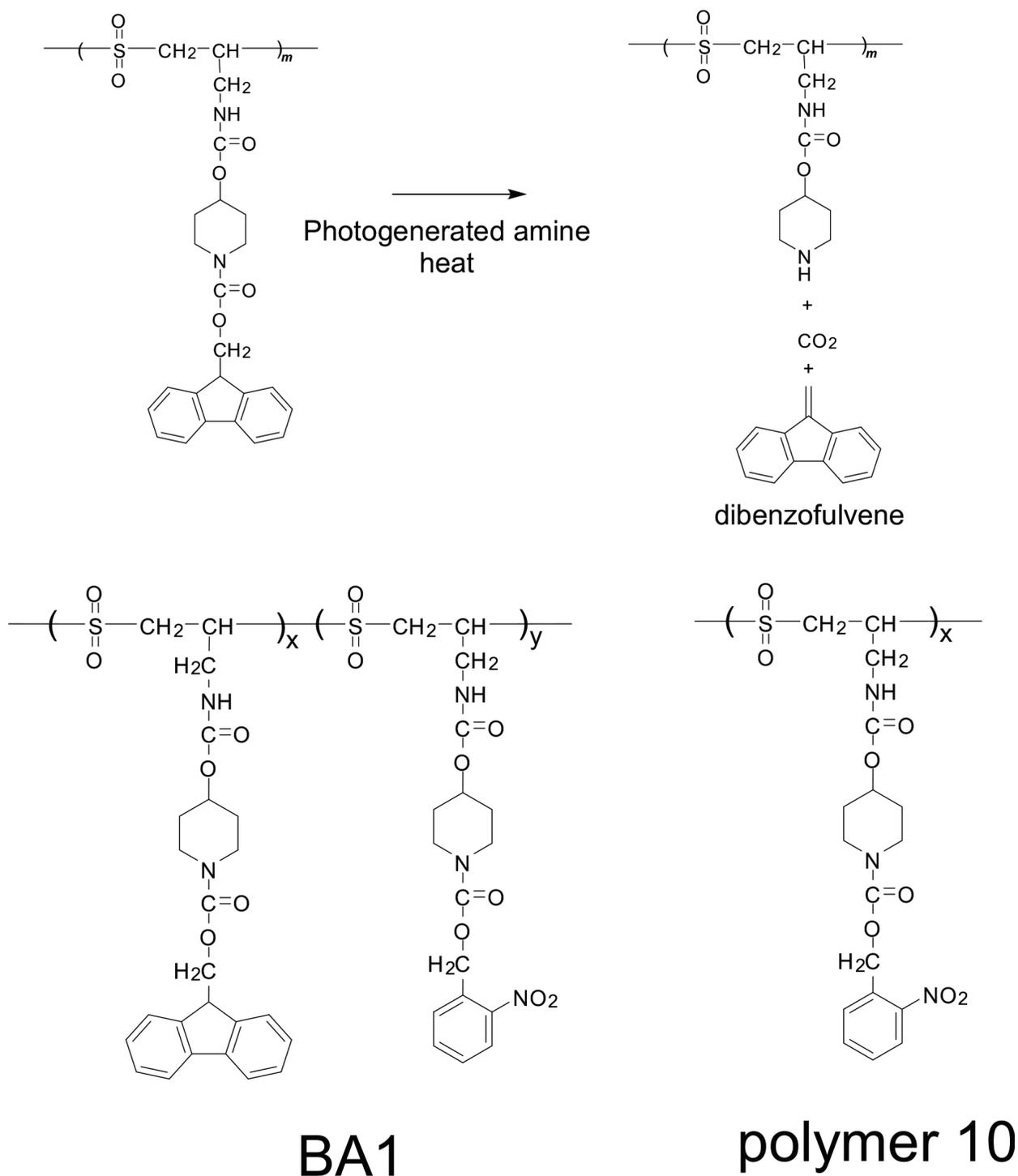


Figure 17. Base amplification mechanism and structures of copolymer BA1 and polymer 10.

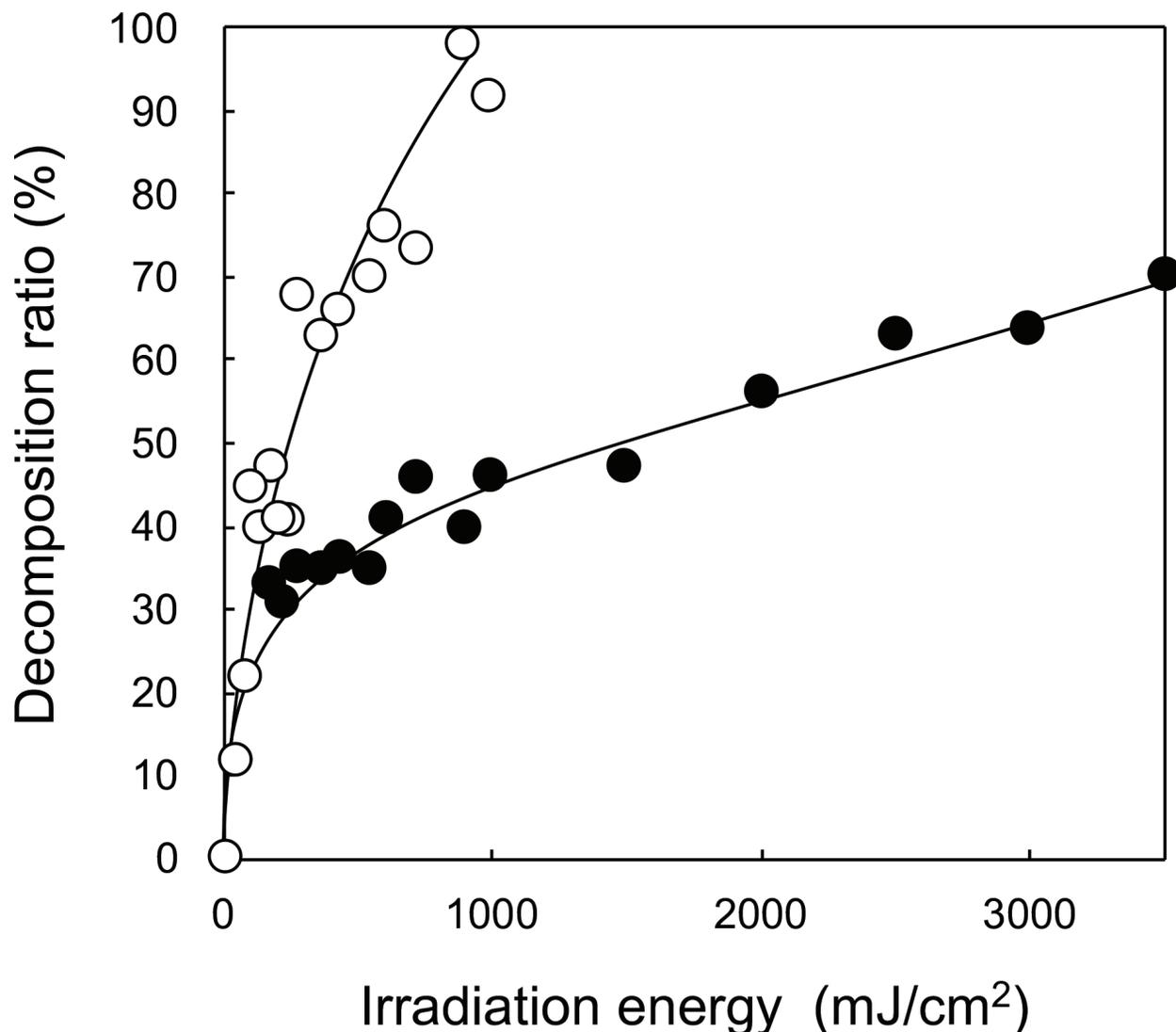


Figure 18. Decomposition ratio of BA1 (○) and polymer 10 (●) as a function of the irradiation energy.

7. Poly(olefin sulfone)s composed of volatile monomers

The photoinduced depolymerization of poly(olefin sulfone)s composed of volatile olefins was investigated [18]. The polymers were converted into volatile compounds by photoinduced depolymerization. A poly(olefin sulfone) film containing a photobase generator (ANC2) was irradiated with 254-nm light at ambient temperature through a photomask. While very little change occurred in the film just after irradiation, the irradiated area of the film vaporized upon heating to 110°C, forming a mask pattern on the film (Figure 19). The surface of the film was also observed by AFM after heat treatment. The results confirmed that the irradiated area was removed, leaving a bare surface. This enables a wide variety of applications, such as stereolithography without the use of solvents, photo-detachable adhesives, and printable nanocircuit fabrication.

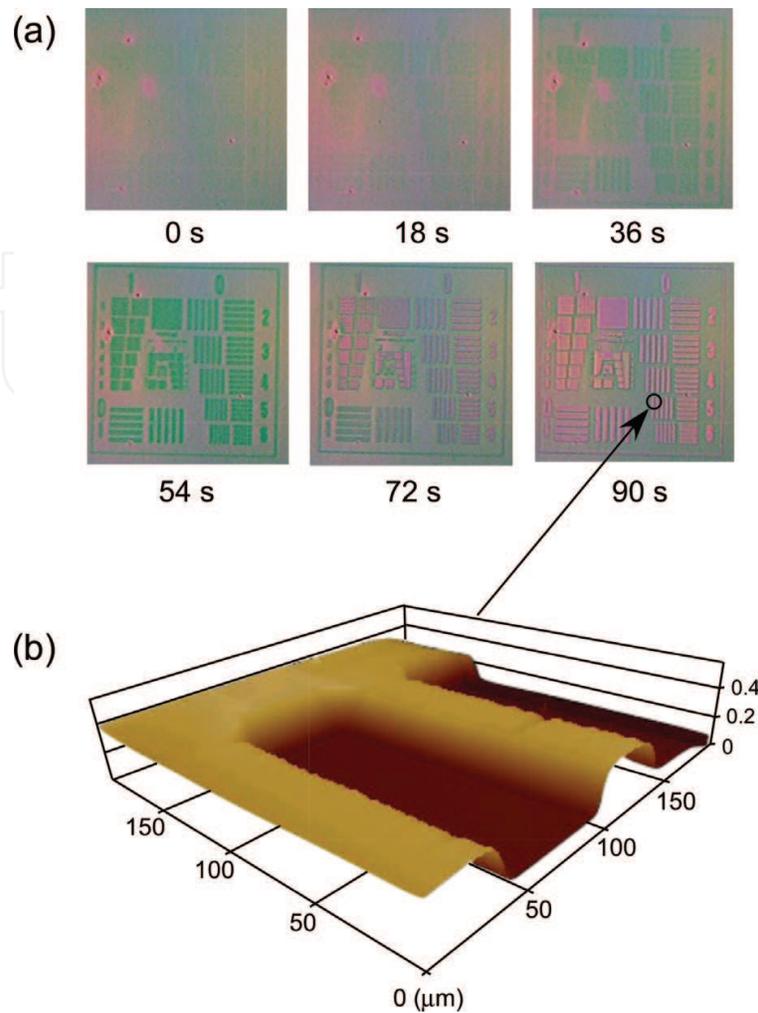


Figure 19. (a) Changes in a photomask pattern irradiated film during heating at 110°C. (b) AFM image of the photomask pattern irradiated area of the PMPs film after heating at 110°C for 15 min.

8. Application of photo-depolymerizable poly (olefin sulfone)s to photo-detachable adhesives

Detachable adhesives have attracted great interest due to their potential applications in reusable products and reworkable systems [22–26]. Adhesives used in many applications, and a variety of strong adhesives that can be employed in extreme environments have been developed [27]. However, most high-performance adhesives are strongly adhesive, making them difficult to remove and therefore cannot be used in recyclable materials or in reworking processes. Therefore, a need exists for glues that provide firm bonding but also can be easily detached. The strength of an adhesive bond essentially depends on surface interactions between the adhesive material and the substrate. Therefore, if the chemical structure of the adhesive material can be changed after adhesion, the adhesion strength may also change. Studies have been reported on the adhesive strength of substrates fastened using degradable polymers [23, 24, 26]. The results showed that depolymerizable polymers can act as detachable adhesives.

The adhesive strength of a poly(olefin sulfone) composed of a volatile olefin monomer and a second olefin monomer possessing a crosslinkable moiety has been evaluated [28]. This polymer was expected to act as a detachable adhesive, as illustrated in **Figure 20**. When a mixture of this poly(olefin sulfone) and a crosslinking reagent was embedded between two glass plates and cured, the plates remained glued together. Subsequently, the glued plates could be separated upon irradiation with UV light and heating. For further investigation, a mixture of the poly(olefin sulfone), a cross-linking agent, and a photobase generator were prepared, and the adhesive strengths before and after photoirradiation were examined. **Figure 21** shows the chemical structures of the samples. The bond strength of the test samples was measured using a cross-tensile test apparatus, shown in **Figure 22**. **Figure 23(a)** shows the tensile strengths obtained from plates bonded with various adhesives: cross-linked TPAS-11, PMPS, a commercially available epoxy adhesive (Araldite Rapid), and polypropylene. The polypropylene did not result in adhesion between the quartz plates, while the cross-linked TPAS-11 clearly possessed a tensile strength greater than those obtained either with the Araldite Rapid or PMPS. The superior bonding strength of the cross-linked TPAS-11 was thought to be due to the highly polar poly(olefin sulfone) main chain and hydrogen bond-

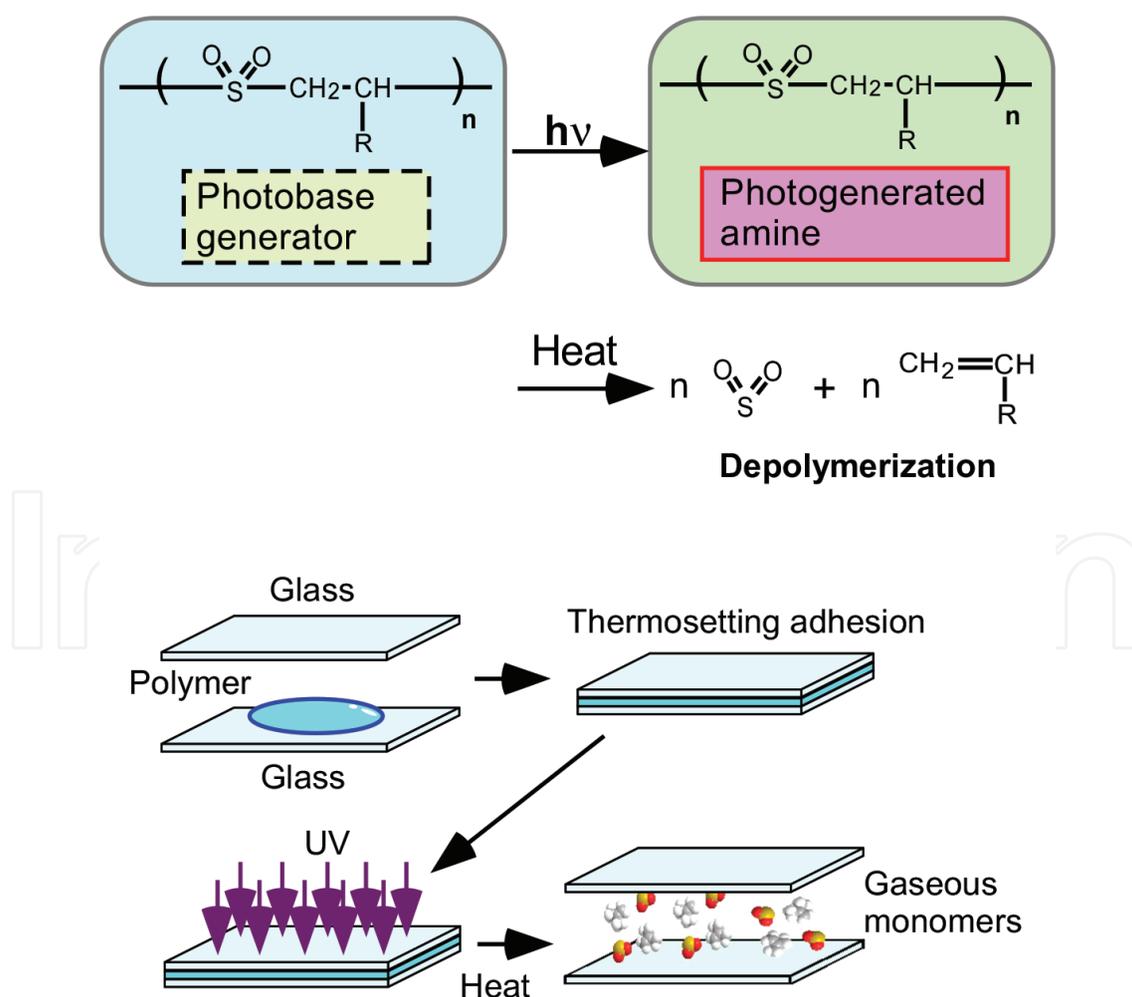


Figure 20. Photoinduced depolymerization of poly(olefin sulfone)s containing photobase generators and a sequence showing a photodetachable thermosetting adhesive.

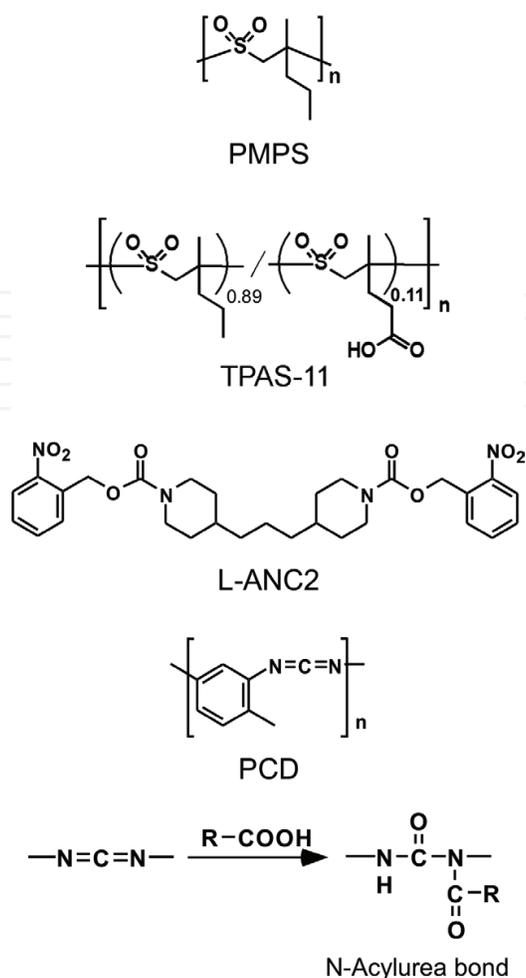


Figure 21. Structures of the poly(olefin sulfone)s (PMPS and TPAS-11), photobase generator (L-ANC2) and crosslinker (PCD) employed in the present study and crosslinking reaction of the carbodiimide PCD and a carboxylic acid.

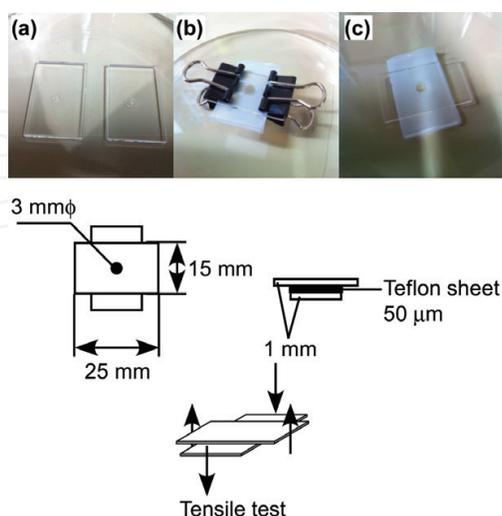


Figure 22. Preparation of samples for adhesion strength measurements: (a) a mixture of TPAS-11, PCD (5 wt%) and L-ANC2 (20 wt%) is placed on quartz plates, (b) the plates are sandwiched on either side of a 50 m Teflon sheet with a 3 mm diameter hole and the assembly heated to 100°C for 10 min, and (c) a finished sample ready for adhesive strength measurements (cross tensile test).

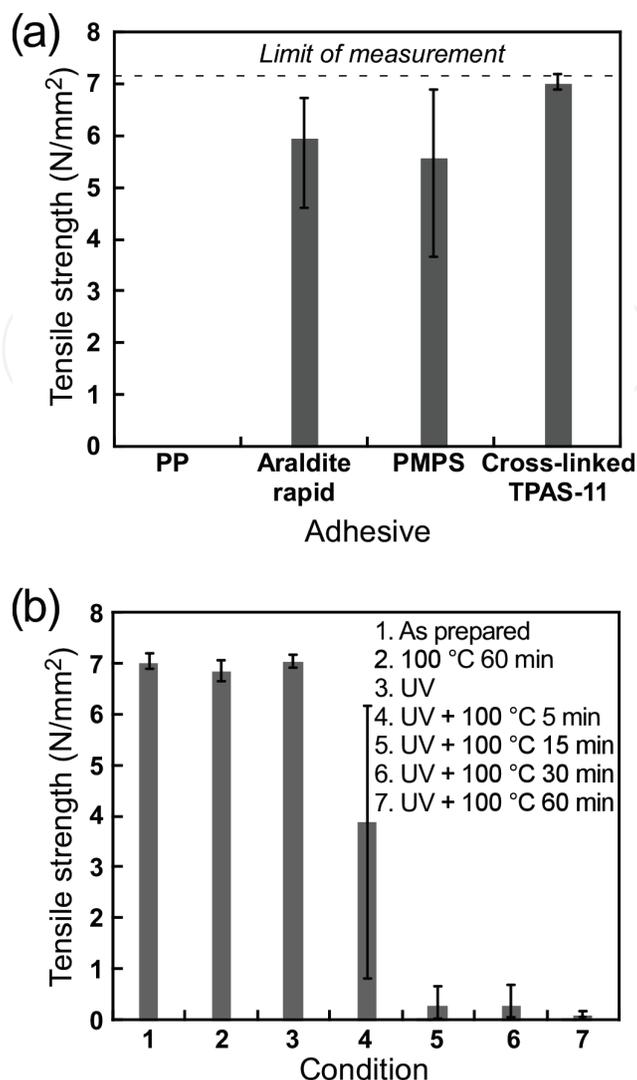


Figure 23. (a) Adhesive strengths of quartz plates bonded with polypropylene (PP), Araldite rapid, PMPS and cross-linked TPAS-11 (with 5 wt% of PCD). Both the PMPS and cross-linked TPAS contained 20 wt% L-ANC2. The maximum tensile strength that could be measured (7.2 N/mm²) is indicated by a dashed line. The tensile test was conducted for 5 times in each measurement. (b) Adhesive strengths of quartz plates bonded with a mixture of TPAS-11, PCD (5 wt%) and L-ANC2 (20 wt%): (1) immediately after sample preparation, (2) after heating at 100°C for 60 min, (3) after irradiation with 254-nm UV light (3.0 J/cm²), (4) after irradiation with UV and heating at 100°C for 5 min, (5) after irradiation with UV and heating at 100°C for 15 min, (6) after irradiation with UV and heating at 100°C for 30 min, and (7) after irradiation with UV and heating at 100°C for 60 min. The tensile test was conducted for 5 times in each measurement.

ing between the carboxylic acid groups and the N-acylurea groups at the cross-linking sites (**Figure 21**). Note that PMPS-glued plates detached upon heating to temperatures above the glass transition temperature of PMPS because it is a thermoplastic resin. In contrast, cross-linked TPAS acted as a thermoset resin and resulted in stable adhesion. The change in the adhesive strength of the cross-linked TPAS-11 upon light irradiation and/or heating was also investigated. **Figure 23(b)** shows the tensile strength of the cross-linked TPAS-11 sample as prepared and after heating at 100°C for 60 min, and upon irradiation with 254-nm UV

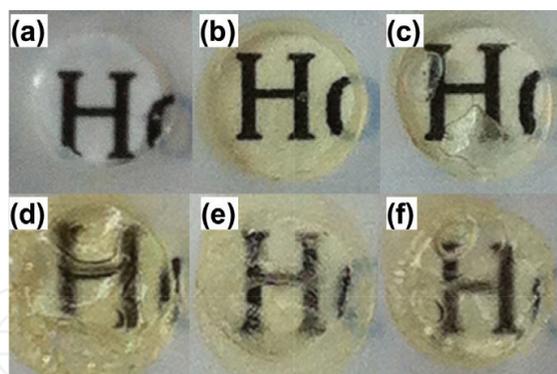


Figure 24. Photographs of a mixture of TPAS-11, PCD (5 wt%) and L-ANC2 (20 wt%): (a) after heating at 100°C for 30 min without UV irradiation, (b) after irradiation with 254-nm UV light (3.0 J/cm²), (c) after UV irradiation and heating at 100°C for 5 min, (d) after UV irradiation and heating at 100°C for 15 min, (e) after UV irradiation and heating at 100°C for 30 min, and (f) after UV irradiation and heating at 100°C for 60 min.

light at 3.0 J/cm², with or without heating for different durations. The results demonstrate that heating before UV irradiation did not weaken the bond strength, while heating after UV irradiation caused the adhesive strength to decrease to nearly zero. **Figure 24** shows photographs of the adhered samples, indicating that the cross-linked TPAS-11 was both colorless and transparent. Following irradiation with UV light, the resin became slightly yellow because of the production of nitrosobenzaldehyde via photodecomposition of L-ANC2. Heating the sample to 100°C also generated gaseous products because of depolymerization of the poly(olefin sulfone), allowing the quartz plates to detach.

9. Conclusions

Photoinduced depolymerization of poly(olefin sulfone)s containing photobase generators was summarized. Since poly(olefin sulfone)s are copolymers of olefins and sulfur dioxide, the sulfur dioxide produced through the depolymerization evaporates from the system. Thus, the depolymerization reaction proceeds only in one direction, and the polymer is converted into consistent olefins. The photoinduced depolymerization of poly(olefin sulfone)s has been investigated for a wide variety of applications, including stereolithography, printable micro-circuit fabrication, and detachable adhesives.

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