

Stability of Poly(*N*-propargylamide)s Under Ultraviolet Irradiation

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ABSTRACT: This article investigates the photostability of poly(*N*-propargylamide)s under different conditions, on the basis of which application research for this class of highly functional polymers can be performed. With helical polymer **1** [monomer: C≡CCH₂NHCOCH(C₂H₅)₂] taken as a representative, some affecting factors, including the ultraviolet (UV)-light intensity, presence of oxygen, far-UV and near-UV light, and temperature, were investigated. It was found that increasing the UV-light intensity accelerated the degradation of polymer **1**. When oxygen was present, it also facilitated the degradation. Far-UV light rather than near-UV light played a predominant role in initiating the degradation of poly-

mer main chains. Elevating the temperature of the polymer solution during UV irradiation made the degradation accelerate. Storing the polymer under weak UV light, in the absence of oxygen, and at a low temperature was favorable for keeping the polymer stable. These findings are important not only from a scientific point of view but especially for developing practical applications of this type of polymer on the basis of its photodegradability. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1924–1931, 2008

Key words: degradation; irradiation; polyacetylenes; radiation

INTRODUCTION

High-quality polyacetylene film exhibiting high electrical conductivity via doping became available with the advent of the Shirakawa method.¹ From then on, the field of substituted polyacetylenes has undergone remarkable developments, and various monosubstituted and disubstituted polyacetylenes have been prepared.^{2,3} The predominant driving force should be ascribed to the unique properties of substituted polyacetylenes, such as liquid crystallinity, photoluminescence, gas and liquid permeability, and chirality and helicity.^{4,5} Despite the great progress in this field, the stability of the synthesized substituted polyacetylenes still seems to be a tough problem, mainly because of the sensitivity of the double bonds in the polymer backbones to oxidation;^{6,7} for cis-rich polyacetylenes, spontaneous cis–trans conformational

transformation may be another reason.^{8,9} Therefore, some studies have been devoted to the degradation behavior of the involved polymers. Tang et al.¹⁰ investigated the radiation effects on silicon-containing monosubstituted and disubstituted polyacetylenes and found that the polymers underwent degradation in air, but *in vacuo*, no polymer degradation took place. Karim et al.¹¹ studied the degradation of stereoregular cis–transoidal polyphenylacetylenes in solution; they found that a cis–transoidal polymer prepared with a rhodium catalyst readily underwent oxidative degradation into oligomers, whereas a polymer with a trans-rich geometrical structure degraded more slowly under the experimental conditions. Simionescu and Percec¹² found that in polyphenylacetylenes, intramolecular cyclization occurred both in solution and in the solid state, by which the polymer main chain was cleaved and 1,3,5-triphenylbenzene was produced. Reportedly, main-chain scission of the polymer could happen at a temperature as low as 20°C.¹³ Upon electron-beam irradiation, *cis*-polyacetylene films showed improved stability according to a report by Roshchupkina et al.⁸ For *cis*-polyacetylenes, cis–trans isomerization readily occurred when the polymers were subjected to γ -ray irradiation¹⁴ or pressure;¹⁵ Ishii et al.¹⁶ particularly explored the characterization of cis–trans isomerization by measuring ¹³C-NMR chemical shifts.

In our earlier studies, a series of poly(*N*-propargylamide)s^{17–22} and poly(*N*-propargylsulfamide)s,²³ two

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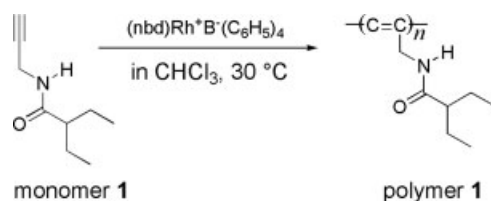
types of substituted polyacetylenes, were synthesized. Among the synthesized polymers, some could form stable helical conformations;¹⁹ others could perform conformational transformations either from a random coil to an ordered helix or from a helix to a random coil.¹⁷ Thus, they possess large promise as candidates for stimuli-responsive materials. Additionally, we studied the thermal stability of poly(*N*-propargylamide)s in solution and in the solid state.²⁴ However, to our knowledge, there have been few studies on the stability of substituted polyacetylenes under ultraviolet (UV) irradiation, except for the report by Tsuchihara et al.,²⁵ in which the degradation and crosslinking of aromatic and alkyl-substituted polyacetylene were examined.

Considering the great importance of polymers' stability to light and especially their potential applications as, for example, optical materials, here we investigate the photostability of poly(*N*-propargylamide)s in detail, using polymer **1** as an example (Scheme 1). The effects of the UV-light intensity, temperature, far-UV and near-UV light, and oxygen were investigated. These investigations are important not only from a scientific point of view but especially for potential industrial applications.

EXPERIMENTAL

Materials

Rhodium catalyst (nbd)Rh⁺B⁻(C₆H₅)₄ (nbd = 2,5-norbornadiene) was synthesized as reported.²⁶ The monomer synthesis and polymerization (Scheme 1) were carried out according to our previous report.¹⁸ Solvents were used without further purification, except tetrahydrofuran (THF), which was used for polymerization and distilled by the standard method. Benzyl dimethyl ketal (Irgacure 651) was purchased from Ciba Specialty Chemicals (Basel, Switzerland). A UV filter (<420 nm; transmittance < 1%) was purchased from Shenzhen Compass Optic Technology Co., Ltd. (Shenzhen, China); poly(ethylene terephthalate) (PET) film (102 μm) was purchased from Baoding Lucky Film Co., Ltd. (Baoding, China); and bioriented polypropylene (BOPP) film (29 μm) was purchased from Beijing 6th Chemical Plant (Beijing, China).



Scheme 1 Chemical structure of polymer **1**.

Measurements

¹H-NMR spectra were recorded on a Bruker AV600 spectrometer (Fallanden, Switzerland). IR spectra were recorded with a Nicolet Nexus 670 spectrophotometer (Madison, WI). Molecular weights and molecular weight distributions of the polymers and products after degradation were determined by gel permeation chromatography (model 150C, Waters) (Milford, MA) calibrated with polystyrenes as standards and THF as an eluent. UV spectra were recorded on a Jasco 810 spectropolarimeter (Tokyo, Japan).

Degradation

Polymer **1** (0.05 g, 0.33 mmol by monomer unit) and THF (30 mL) were added to a 100-mL, flat-bottom quartz reactor (self-made); the reactor was tightly covered with a BOPP film to prevent the solvent from evaporating. It was proved that the BOPP film did not absorb UV light and allowed over 95% of the light to pass through it. After the polymer dissolved completely, the reactor was placed in a water bath of a certain temperature. UV irradiation was performed with a high-pressure mercury lamp (375 W) as a light source. After irradiation, the reactor was taken off the bath, and the product was subjected to further characterization. To investigate the effects of oxygen, the polymer solution was first bubbled with nitrogen for 20 min and then UV-irradiated under nitrogen. To investigate the influence of UV-light intensity, the distance between the light source and the reactor was adjusted appropriately. To investigate the effects of far-UV and near-UV light, a light filter was used to exclude nearly all the UV light below 420 nm, and a PET film covering the polymer solution could filter out the far-UV light and allow only UV light with wavelengths above 300 nm to pass through it.

Characterization

With THF as a solvent, the irradiated polymer solutions were directly subjected to gel permeation chromatography. To obtain the ¹H-NMR spectrum, polymer **1** was dissolved in CDCl₃, irradiated by UV radiation, and then subjected to NMR measurement. The obtained dry products were dissolved in THF to measure the ultraviolet–visible (UV–vis) spectrum and dissolved in different solvents to examine the products' solubility. Dry products were used directly to measure the IR spectrum (with KBr discs).

RESULTS AND DISCUSSION

Effects of light intensity and oxygen

Polymer **1** was irradiated by UV light with intensities of 16 and 24 W/m² (measured at a wavelength

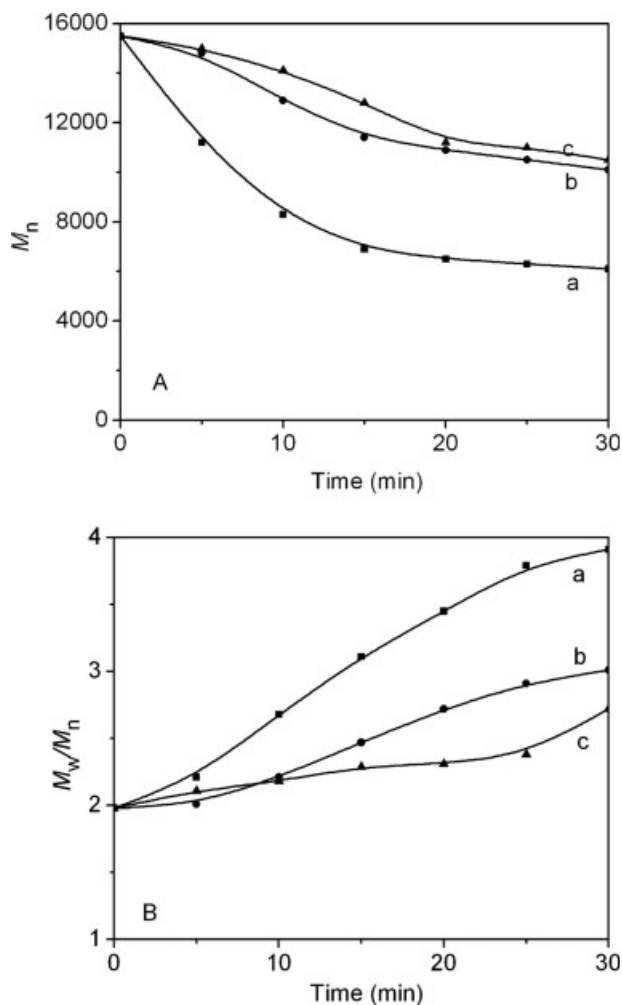


Figure 1 Effects of the UV-light intensity on the degradation of polymer 1 in THF (concentration = 0.011M at room temperature): (A) M_n and (B) M_w/M_n . The light intensity (at 297 nm) was (a) 24 W/m² under air, (b) 16 W/m² under air, and (c) 24 W/m² under nitrogen.

of 297 nm), and the influence of the different light intensities is presented in Figure 1. As shown in Figure 1(a), the number-average molecular weight (M_n) decreased in both cases, especially at the beginning of irradiation; in comparison, the stronger the light intensity was, the more rapidly M_n decreased under the experimental conditions. For example, when the polymer was irradiated for 5 min, its M_n decreased from the original value of 16,000 to 15,000 with the light intensity being 16 W/m², but for the same irradiation period and the same initial polymer sample, M_n decreased to 11,000 with the light intensity being 24 W/m². When the polymer was irradiated for 30 min, M_n decreased to about 10,000 for the former (16 W/m²), and it decreased to 6100 for the latter (24 W/m²). In Figure 1(b), the change in the molecular weight dispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n)] is shown as a function of the irradiation time. Just

like the results for M_n presented in Figure 1(a), stronger light intensity (24 vs 16 W/m²) gave rise to a more pronounced change in M_w/M_n [Fig. 1(b)]. These results clearly demonstrated that strong UV radiation accelerated the degradation of the polymer. It can be inferred that storing the polymer under weak light, especially weak UV light, is favorable for keeping the polymer stable for a longer period. Reportedly, González-Velasco et al.⁷ found that sunlight strongly accelerated the degradation of poly(2-hexyne) films.

Previous studies told us that polymer 1 could form stable helices,¹⁸ and thus the ability of polymer 1 to form helices was examined before and after UV irradiation in this research. The relevant results are presented in Figure 2. It was already known that for *N*-propargylamide polymers, the appearance of a strong UV absorption band at about 400 nm indicated the formation of a helical conformation; otherwise, the strong UV absorption peak appearing around 320 nm would indicate the formation of a

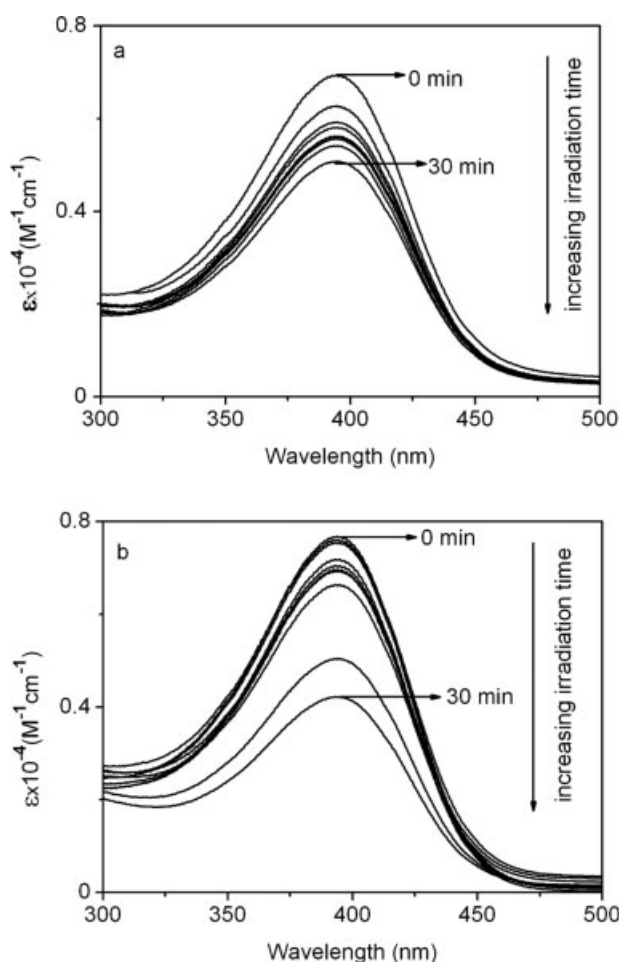


Figure 2 Effects of the UV-light intensity on the UV spectra of polymer 1 in THF (concentration = 0.011M, at room temperature under air). The light intensity (297 nm) was (a) 16 and (b) 24 W/m².

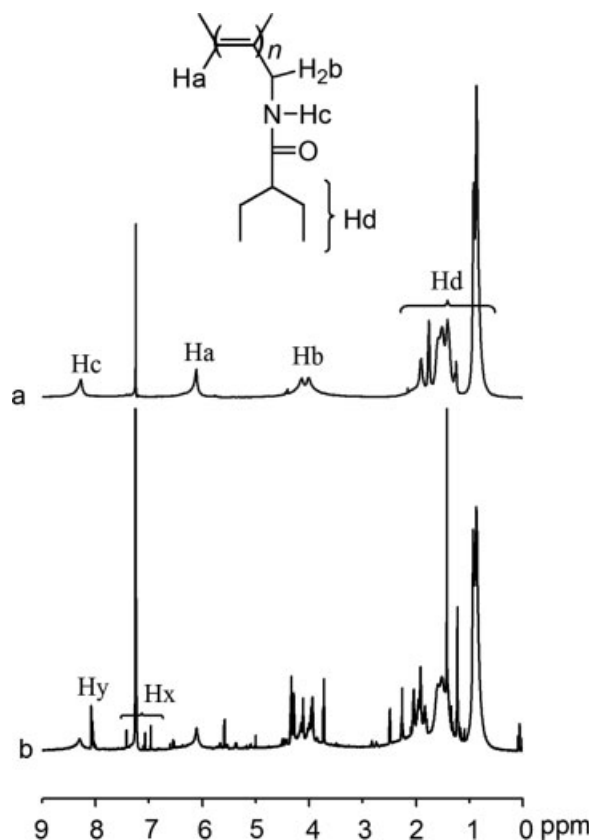


Figure 3 $^1\text{H-NMR}$ spectra of polymer 1 before and after UV irradiation (measured in CDCl_3 at room temperature): (a) the initial sample of polymer 1 and (b) polymer 1 UV-irradiated with a light intensity of 24 W/m^2 (297 nm) for 30 min.

random coil in the polymer main chains.^{17–22} In Figure 2(a), the UV intensity is 16 W/m^2 , and the irradiation time ranges from 0 to 30 min; in Figure 2(b), the UV intensity increases to 24 W/m^2 . Before irradiation, the extinction coefficient at 390 nm ($\epsilon_{390\text{nm}}$) of the original polymer was about $7000 \text{ M}^{-1} \text{ cm}^{-1}$; after irradiation for 30 min, $\epsilon_{390\text{nm}}$ decreased to about $5000 \text{ M}^{-1} \text{ cm}^{-1}$ with UV light of 16 W/m^2 in intensity [Fig. 2(a)]. It decreased to $4000 \text{ M}^{-1} \text{ cm}^{-1}$ when the UV intensity changed to 24 W/m^2 [Fig. 2(b)]. The different values of $\epsilon_{390\text{nm}}$ correspond to the different helix contents in the involved polymers;^{17–22} the results in Figure 2 thus suggest that the helix content decreased along with UV irradiation, indicating the cleavage of the polymer main chains when these results are considered together with Figure 1. These data provide indirect evidence for the occurrence of degradation in the polymer main chains. According to our earlier studies,²⁴ the decrease in the molecular weight should be accompanied by a decrease in the cis content. This was verified by the measurement of the cis content^{17–22} of the polymer main chains before and after UV irradiation. For example, for the sample irradiated for 30 min in Fig-

ure 1, the cis content before irradiation was 100%, and it decreased to only 81% after irradiation. As shown in Figure 2, the polymer did not exhibit a helix to random coil conformational transition because no absorption peak appeared around 320 nm, whereas the absorption peak at 390 nm decreased gradually.

In Figure 1, the effects of oxygen are also presented, with the UV-light intensity being 24 W/m^2 . As shown in Figure 1(a), irradiation under nitrogen prevented the polymer from degrading to a certain degree; this was reflected by the slight change in M_n in comparison with the data obtained in the presence of oxygen. M_w/M_n , as shown in Figure 1(b), also changed slightly for the polymer protected by nitrogen during irradiation. These results indicate that the presence of oxygen during irradiation facilitated the polymer degradation. Nevertheless, they also suggest that even protected by nitrogen, the polymer still underwent degradation but at a much slower rate. This finding is in good agreement with the observations in earlier research focused on the thermal degradation behavior of poly(*N*-propargylamide)s.²⁴ It was also reported by Matsunami et al.²⁷ that cis-rich polyphenylacetylene exhibited a decrease in its molecular weight through a thermal treatment in the presence of nitrogen.

Furthermore, with reference to our preceding report,²⁴ it can be inferred that oxygen participated in the degradation of the polymer. To make this clear, $^1\text{H-NMR}$ and IR spectra of the resulting product were recorded, as shown in Figures 3 and 4.

In Figure 3(a) (the original polymer), the signals at 0.75–1.90, 3.91–4.11, 6.10, and 8.22 ppm should be assigned to the corresponding hydrogens presented in the figure.¹⁸ In Figure 3(b), some new signals appear for the products after degradation. Because of the complexity of the products, it is quite difficult to precisely analyze the newly appearing signals; however, the signals at 7.00–7.45 ppm (Hx) could be assigned to aromatic hydrogens, and the signal at about 8.00–8.09 ppm (Hy) seems to be assignable to the hydrogens in polar groups in the products after degradation. The aforementioned reasoning that the new signals at 7.00–7.45 ppm should be assigned to aromatic hydrogens was proposed by Percec et al.,²⁸ several other investigations also provided evidence for it.^{29,30}

Figure 4 presents the IR spectra of polymer samples before and after degradation. In comparison with the IR spectrum of the original polymer [Fig. 4(a)], new bands clearly appear, especially at about 1172 and 1727 cm^{-1} . Here, it is assumed that these new bands should be assigned to $-\text{CHO}$ groups in the degraded product; the newly appearing signals in $^1\text{H-NMR}$ in Figure 3 also provide evidence for this reasoning. Therefore, it seems reasonable to

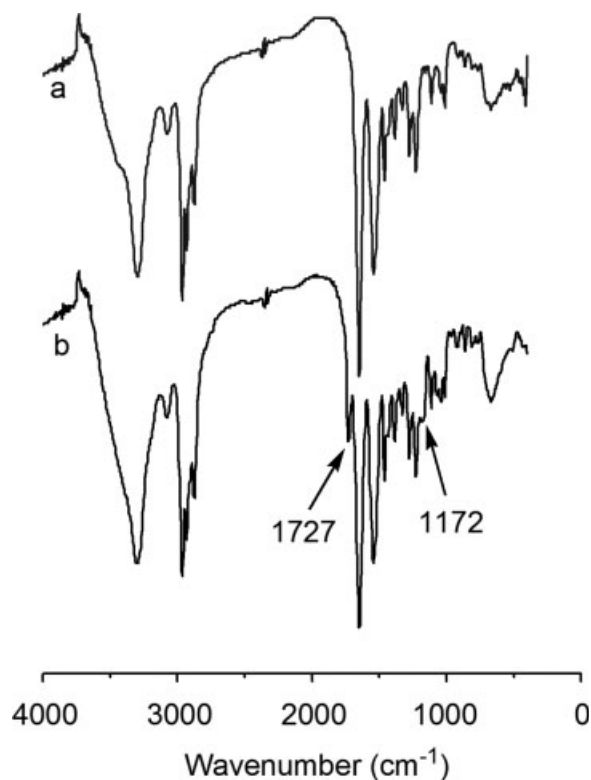


Figure 4 IR spectra of polymer **1** before and after UV irradiation (measured with KBr discs): (a) the initial sample of polymer **1** and (b) polymer **1** UV-irradiated with a light intensity of 24 W/m^2 (297 nm) for 30 min.

draw the conclusion that oxygen took part in the degradation of the polymer; moreover, the presence of oxygen accelerated the degradation. If this assumption is true, the products after degradation should show somewhat improved solubility in polar solvents. This was also clarified by an examination of the solubility of the products in polar and nonpolar solvents, as summarized in Table I.

The original polymer **1** dissolved thoroughly only in THF, CHCl_3 , and CH_2Cl_2 ; in the other solvents listed in Table I, it hardly dissolved. However, it is clear in Table I that the products after degradation could partly dissolve in solvents other than THF, CHCl_3 , and CH_2Cl_2 , including acetyl acetate, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and methanol. In a reference experiment, we examined the solubility of polymer **1** with a low molecular weight ($M_n = 4500$, $M_w/M_n = 2.11$), and

it was revealed that this polymer hardly dissolved in the solvents, including acetyl acetate, DMF, DMSO, and methanol. These phenomena provided indirect support for the conclusion that oxygen took part in the degradation of polymer **1** mentioned previously.

Effects of near-UV and far-UV light

Our previous studies dealing with photografting polymerization showed that near-UV and far-UV light played different roles in initiating photografting polymerizations.^{31–33} Thus, in this study, we also explored the effects of near-UV and far-UV light on the degradation behavior of polymer **1**. The results are shown in Figure 5.

A light filter and a PET film were used to protect the polymer solution from the irradiation of UV light and far-UV light, respectively, because the light filter was opaque to all the UV light ($<420 \text{ nm}$; transmittance $< 1\%$) and the PET film allowed only the near-UV light to pass through it ($<300 \text{ nm}$; transmittance $< 5\%$). As shown in Figure 5(a), when the PET film was used, M_n of polymer **1** decreased at a much lower rate than M_n of the polymer without the PET film; using the light filter made M_n decrease at an even slower speed. As shown in Figure 5(b), the use of either the PET film or light filter made the increase in M_w/M_n not as noticeable as that without the use of the PET film or light filter. As expected, the helix content in the polymer after irradiation exhibited only a slight decrease when the PET film and light filter were present (the figures were omitted). On the basis of these results, we can reasonably conclude that far-UV light rather than near-UV light made a predominant contribution to the degradation of the polymer. This finding is consistent with the investigations on photografting polymerization previously reported by us.^{31–33}

Effects of temperature

The thermal degradation behavior of poly(*N*-propargylamide)s had been investigated earlier by us.²⁴ In addition, it had been demonstrated that enhancing the temperature facilitated photoinduced reactions, such as photografting polymerization, because it increased the reactivity of the active species in the examined systems.^{34,35} In this research, the influence

TABLE I
Solubility of Polymer **1** Before and After Irradiation

Solvent	DMF	DMSO	THF	CH_2Cl_2	CHCl_3	Acetyl acetate	Methanol
Before irradiation	×	×	○	○	○	×	×
After irradiation	□ (85%)	□ (80%)	○	○	○	□ (45%)	□ (55%)

The solubility of each polymer sample (2 mg) in the solvent (1 mL) was examined at room temperature; the data in parentheses indicate the approximate solubility of the polymer. ○ = soluble; □ = partly soluble; × = insoluble.

of temperature was also investigated, and the results are presented in Figure 6. When the temperature was increased from 30 to 45°C, both M_n [Fig. 6(a)] and M_w/M_n [Fig. 6(b)] increased in the same order for the same irradiation time. For example, for the samples irradiated for 30 min, at 30°C, M_n was 10,100, and M_w/M_n was 3.01; at 35°C, they were 6500 and 3.33; at 40°C, they increased to 5100 and 3.92; and at 45°C, they further increased to 3500 and 5.11, respectively. These results show that even in the degradation induced by UV light, the temperature was an important factor, and irradiation at a high temperature could facilitate the degradation of the polymer.

Effects of the photoinitiator

On the basis of the aforementioned results, the photodegradation of polymer 1 was mainly due to the

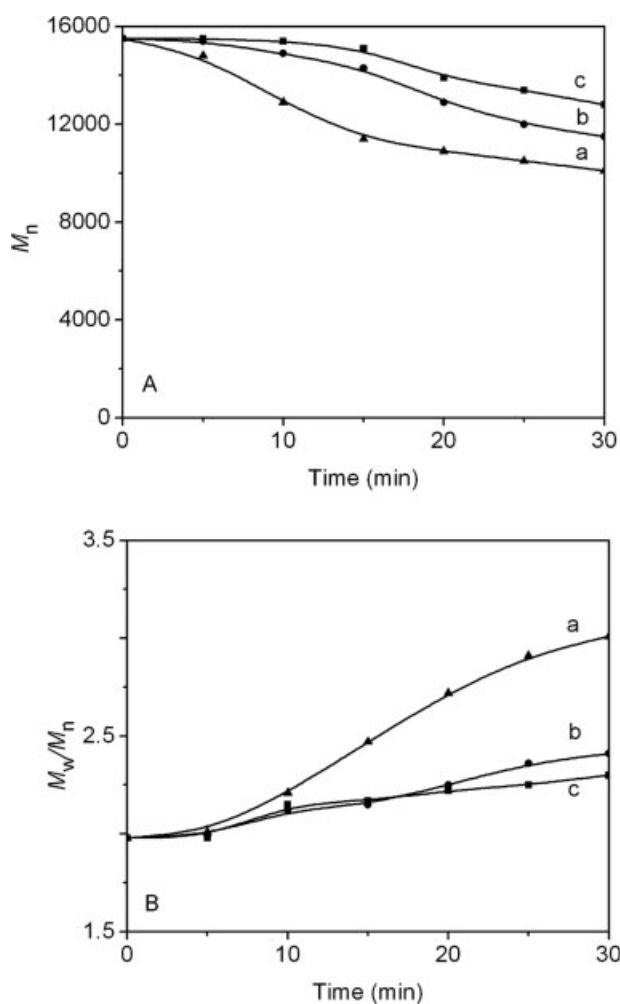


Figure 5 Roles of far-UV light in the degradation of polymer 1 in THF (concentration = 0.011M, at room temperature under air, 16 W/m²) (a) without a filter and PET film, (b) with a PET film, and (c) with a light filter: (A) M_n and (B) M_w/M_n .

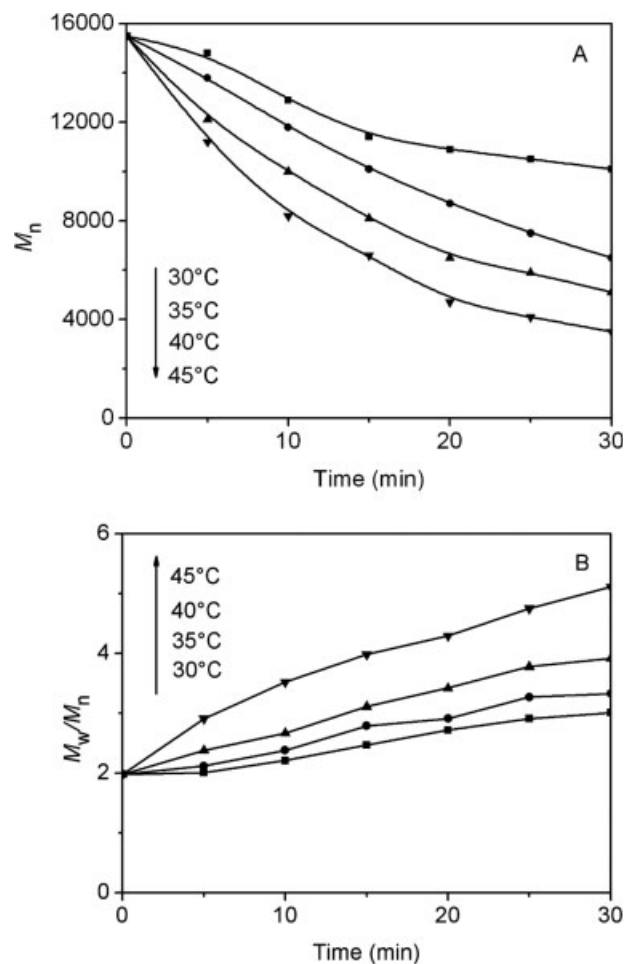


Figure 6 Effects of temperature on the degradation of polymer 1 in THF (concentration = 0.011M, under air, 16 W/m²): (A) M_n and (B) M_w/M_n .

far-UV light, with other conditions kept unchanged. When a photoinitiator is added to a solution of the polymer during UV irradiation, maybe it can inhibit the degradation of the polymer, especially when the extinction coefficient (ϵ) of the photoinitiator in the far-UV range is much higher than that of the polymer. This assumption was examined in this research; however, the experiments gave the opposite results, as presented in Figure 7.

In comparison with the original sample, adding the photoinitiator (Irgacure 651) resulted in a more drastic decrease in M_n and an increase in M_w/M_n . This indicates that Irgacure 651 made the degradation occur with much more ease. We propose that when exposed to UV irradiation, Irgacure 651 absorbed the UV light below 300 nm (Fig. 8) and underwent chain cleavage forming two free radicals; the radicals could attack the polymer main chains by abstracting hydrogens, giving rise to a number of free radicals in the polymer main chains. Then, the subsequent degradation reactions followed the degradation mechanism in the absence of a photoinitia-

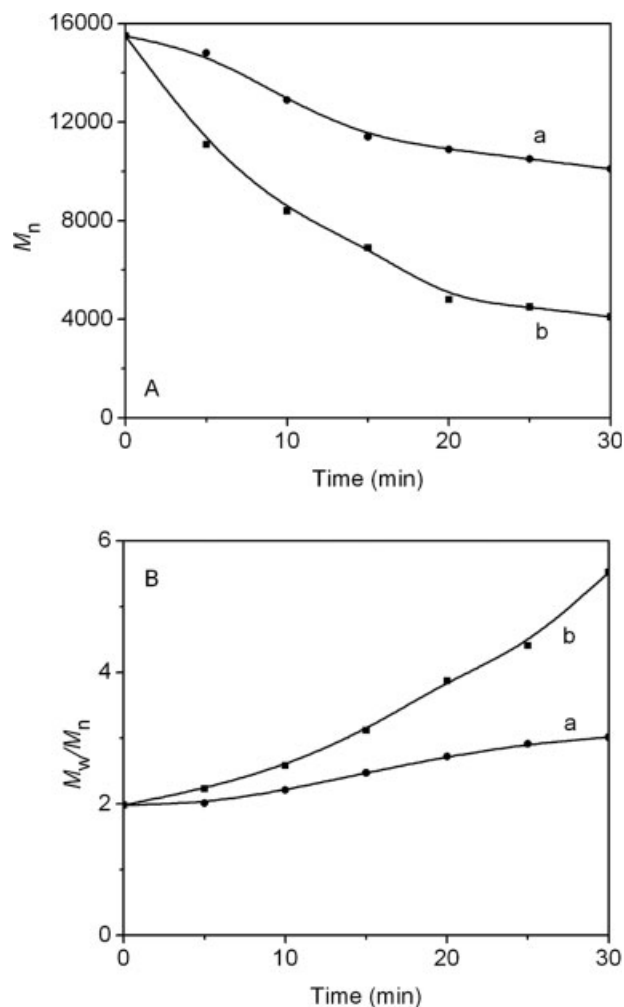


Figure 7 Effects of (a) the absence of Irgacure 651 and (b) the presence of Irgacure 651 on the degradation of polymer 1 in THF (concentration = 0.011M, at room temperature under air, 16 W/m²): (A) M_n and (B) M_w/M_n .

tor. These findings tell us that the addition of a photoinitiator, at least a Norrish type I photoinitiator, exerts negative effects on the stability of the polymer when it is exposed to UV light, even though the exact mechanism is not understood yet.

Another point worthy of note is that, in all the experiments, crosslinking of the polymer chains was not observed according to the data for M_n and the solubility of the products after UV irradiation. This is quite different from the reports about polyacetylenes by Tsuchihara et al.²⁵ On the basis of the aforementioned investigations together with earlier reports from us²⁴ and others,²⁸ the main degradation processes are proposed in Scheme 2 (R is the substituent group in polymer 1; HR' is the available C—H bonds in the polymer). The possible mechanism for isomerization and the formation of products bearing aromatic groups are also outlined in Scheme 2.

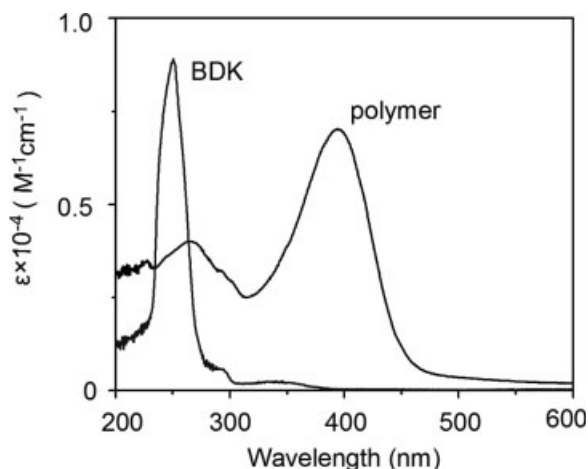
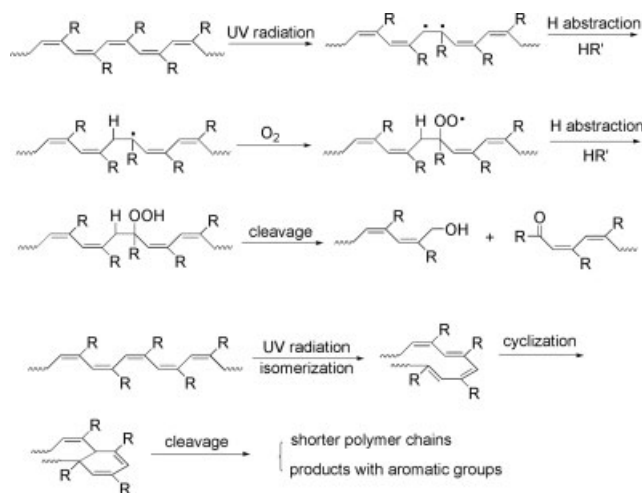


Figure 8 UV-vis spectra of Irgacure 651 and polymer 1 in THF (concentration = 0.1 mM) measured at room temperature.

CONCLUSIONS

With polymer 1 as a representative, the stability of *N*-propargylamide polymers under UV irradiation was investigated. Enhanced light intensity led to accelerated degradation, which was demonstrated by a sharp decrease in M_n , an increase in M_w/M_n , and a decrease in the helix content in the degraded polymer. In the presence of oxygen, the degradation occurred more quickly than under nitrogen; furthermore, oxygen took part in the degradation reactions. The far-UV light made the predominant contribution to the degradation behavior. Elevating the temperature during UV irradiation enabled the degradation to occur more rapidly. Adding a photoinitiator could not prevent the polymer from degrading and even facilitated degradation. The investigations in this research are useful for the design of highly degrad-



Scheme 2 Main degradation processes of polymer 1 under UV irradiation.

able functional polymeric materials, such as photore-sists, because of the photodegradability of the poly-mers.

References

1. Shirakawa, H. *Angew Chem Int Ed* 2001, 40, 2574.
2. Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem Rev* 2000, 100, 1645.
3. Lai, C. M.; Meng, H. F. *Phys Rev B* 1996, 54, 16365.
4. Masuda, T.; Sanda, F. *Handbook of Materials*; Wiley-VCH: Weinheim, 2003; Vol. 3.
5. Lam, J. W. Y.; Tang, B. Z. *Acc Chem Res* 2005, 38, 745.
6. González-Velasco, J. R.; González-Marcos, J. A.; Delgado, J. A. *J Membr Sci* 1997, 129, 83.
7. González-Velasco, J. R.; González-Marcos, J. A.; Delgado, J. A.; González-Ortiz, de, E. C.; Gutiérrez-Ortiz, J. I. *Chem Eng Sci* 1996, 51, 1113.
8. Roshchupkina, O. S.; Tkachenko, L. I.; Efimov, O. N. *Synth Met* 1997, 90, 89.
9. Simionescu, C. I.; Percec, V. *Prog Polym Sci* 1982, 8, 133.
10. Tang, B. Z.; Masuda, T.; Higashimura, T. *J Polym Sci Part A: Polym Chem* 1989, 27, 1197.
11. Karim, S. M. A.; Nomura, R.; Masuda, T. *J Polym Sci Part A: Polym Chem* 2001, 39, 3130.
12. Simionescu, C. I.; Percec, V. *J Polym Sci Polym Chem Ed* 1980, 18, 147.
13. Sedlacek, J.; Pacovska, M.; Etrych, T.; Dlouhy, M.; Pater, N.; Cabioch, S.; Lavastre, O.; Balcar, H.; Zigon, M.; Vohlidal, J. *Polym Mater Sci Eng* 1997, 77, 52.
14. Kozuka, M.; Sone, T.; Tabata, M.; Sadahiro, Y.; Enoto, T. *Radiat Phys Chem* 2002, 63, 59.
15. D'Amato, R.; Sone, T.; Tabata, M.; Sadahiro, Y.; Vittoria, M.; Furlani, A. *Macromolecules* 1981, 31, 8660.
16. Ishii, F.; Matsunami, S.; Shibata, M.; Kakuchi, T. *J Polym Sci Part B: Polym Phys* 1999, 37, 1657.
17. Deng, J. P.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* 2004, 37, 1891.
18. Deng, J. P.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* 2004, 37, 5149.
19. Deng, J. P.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* 2004, 37, 7156.
20. Deng, J. P.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* 2004, 37, 9715.
21. Deng, J. P.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromol Chem Phys* 2004, 205, 1103.
22. (a) Deng, J. P.; Wang, J. M.; Zhao, W. G.; Zhang, Z. G.; Yang, W. T. *Macromol Chem Phys* 2007, 208, 316 (b) Deng, J. P.; Zhao, W. G.; Wang, J. M.; Zhang, Z. G.; Yang, W. T. *Macromol Chem Phys* 2007, 208, 218.
23. (a) Deng, J. P.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* 2004, 37, 5538 (b) Zhang, Z. G.; Deng, J. P.; Zhao, W. G.; Wang, J. M.; Yang, W. T. *J Polym Sci Part A: Polym Chem* 2007, 45, 500.
24. Deng, J. P.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Polymer* 2004, 45, 7395.
25. Tsuchihara, K.; Masuda, T.; Higashimura, T. *J Polym Sci Part A: Polym Chem* 1991, 29, 471.
26. Schrock, R. R.; Osborn, J. A. *Inorg Chem* 1970, 9, 2339.
27. Matsunami, S.; Watanabe, T.; Kamimura, H.; Kakuchi, T.; Ishii, F.; Tsude, K. *Polymer* 1996, 37, 4853.
28. Percec, V.; Rudick, J. G.; Nombel, P.; Buchowicz, W. *J Polym Sci Part A: Polym Chem* 2002, 40, 3212.
29. Kong, X.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* 1999, 32, 1722.
30. Matsunami, S.; Kakuchi, S.; Ishii, F. *Macromolecules* 1997, 30, 1074.
31. Deng, J. P.; Yang, W. T.; Rånby, B. *Eur Polym J* 2002, 38, 1449.
32. Deng, J. P.; Yang, W. T. *J Polym Sci Part A: Polym Chem* 2001, 39, 3246.
33. Yang, W. T.; Rånby, B. *Polym Bull* 1996, 37, 89.
34. Deng, J. P.; Yang, W. T.; Rånby, B. *J Appl Polym Sci* 2000, 77, 1513.
35. Deng, J. P.; Yang, W. T. *J Appl Polym Sci* 2003, 87, 2318.