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Radical polymerization of styrene mediated by 1,3,5-triphenylverdazyl

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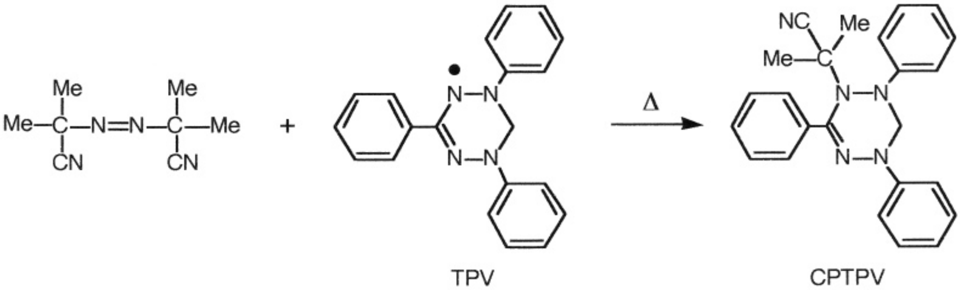
Abstract
2-(2-cyano-2-propyl)-1,3,5-triphenyl-1,2,5,6-tetrahydro-1,2,4,5-tetrazine dissociating into 1,3,5-triphenylverdazyl (TPV) and 2-cyano-2-propyl radical on heating was employed as the unimolecular initiator for the “living” free radical polymerization of styrene in the hope that TPV can be the mediator for the living polymerization. The polymerization followed first order kinetics with respect to styrene and the $\overline{M}_n$ of the resultant polymer increased with increasing conversion. However, the contents of end groups and $\overline{M}_w/\overline{M}_n$ of the polymers indicated that the propagating radicals reversibly coupled with TPV and a rapid decrease in the TPV concentration arising from thermal decomposition allows concurrence of bimolecular termination leading to $\overline{M}_w/\overline{M}_n > 1.5$.

Introduction

The nitroxide mediated “living” free radical polymerization of styrene (St) has drawn much attention because of the molecular weight control and narrow molecular weight distribution (1). Among the nitroxides examined, 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) is one of the most important mediators. Some other nitroxides have also been examined as the mediator of the “living” freer radical polymerization. However, the effect of the structural change in the nitroxide on the living radical polymerization seems to be related to several factors, and as a result, finding of a mediator as effective as or more effective than TEMPO is not an easy task (2-5). It is worthwhile to examine a stable free radical other than nitroxide as the mediator.

1,3,5-Triphenylverdazyl (TPV) (6) has been conveniently used as a scavenger for the determination of initiation rate (7), a quantitative scavenger for the propagating radical of diisopropyl fumarate (8), and a reference radical for ESR quantification of propagating radicals (9). Furthermore, it is known that TPV couples with various carbon centered



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radicals including primary radicals from azo initiators and that some of the coupling products are thermally labile to regenerate TPV upon heating at 40 °C or above (10,11).

We have employed the coupling products of TPV as initiators of the polymerizations of St up to 80 °C in the hope that the coupling product with the propagating radical is also thermally labile and regenerates the propagating radical (12). However, no experimental results could evidence for the significant dissociation of the C-N bond between the PSt chain end and TPV moiety during the St polymerization. It was concluded that the polymerization temperature is too low to cleave significantly the C-N bond because the "living" free radical polymerization involving the equilibrium between active propagating radical and dormant species at 100 °C or above was not known.

In the present work, we reexamined the coupling product of TPV with the 2-cyano-2-propyl radical generated from 2,2'-azobisisobutyronitrile (AIBN) as the unimolecular initiator of the "living" free radical polymerization of St at 90 °C or above.

Experimental

TPV was synthesized according to a previously reported method (6). 2-(2-Cyano-2-propyl)-1,3,5-triphenyl-1,2,5,6-tetrahydro-1,2,4,5-tetrazine (CPTPV), was prepared by the decomposition of AIBN in the presence of TPV in refluxing benzene (10,11). St was distilled under reduced pressure before use. The polymerizations were run in sealed tubes. After polymerization for a certain period, the contents of each tube were poured into an excess amount of methanol to precipitate the polymer. The ^{1}H- and ^{13}C-NMR spectra were recorded using a JEOL a-400 spectrometer. Deuteriochloroform and tetramethylsilane were used as the solvent and the internal standard, respectively. $\overline{M}_w$ and $\overline{M}_n$ were measured by a Tosoh 8200 HLPC equipped with columns for GPC. ESR spectra were taken by a Bruker ESP 300 and *tert*-butylbenzene was used as the solvent.

Results and Discussion

The polymerization of St using different amounts of CPTPV at 110 °C approximately followed first order kinetics as shown by the dotted line in Fig. 1. The polymerization

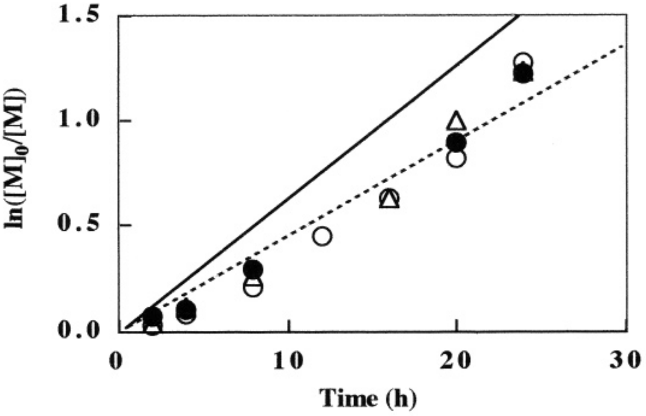


Fig. 1. First-order kinetic plot for St polymerization initiated with CPTPV at 110 °C: [CPTPV] = 6 (●), 12 (△), and 24 mmol/L (○). Solid and dotted lines show first order plots for thermal and CPTPV initiated polymerizations, respectively.

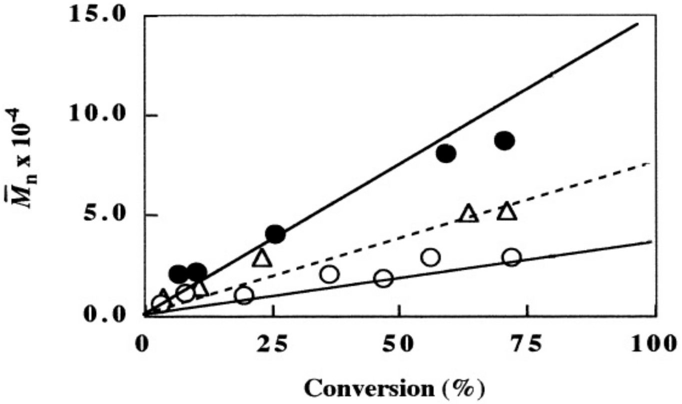


Fig. 2. $\bar{M}_n$ vs. conversion plot for St polymerization initiated with CPTPV at 110 ℃: [CPTPV] = 6 (●), 12 (△), and 24 mmol/L (○). Solid and dotted lines show the theoretical $\bar{M}_n$ calculated from the concentration of St polymerized and CPTPV.

rate, which remained almost constant irrespective of the amount of CPTPV, is slightly lower than the thermal polymerization rate (13) as well as the TEMPO mediated polymerization (14). An increase in conversion resulted in an increase in the rate of the CPTPV initiated polymerization which was closer to that of thermal polymerization.

An increase in $\bar{M}_n$ with increasing conversion is one of the requirements for the "living" free radical polymerization. Fig. 2 illustrates the increases in $\bar{M}_n$ with conversion at different CPTPV concentrations. The experimental results are close to the $\bar{M}_n$ calculated from the concentrations of polymerized monomer and CPTPV concentration as shown by the solid or dotted line. A lower concentration of CPTPV resulted in a higher $\bar{M}_n$, indicating that fewer polymer chains were produced from a lower concentration of CPTPV. The increase in $\bar{M}_n$ with conversion could be explained by the reversible dissociation of the C-N bond followed by propagation of the active radical. However, as

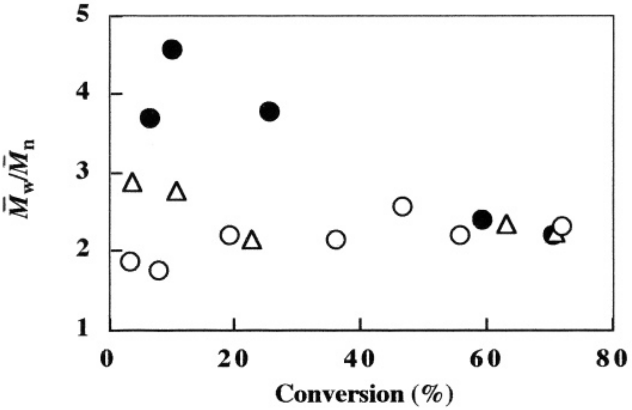


Fig. 3. Conversion vs. $\bar{M}_w/\bar{M}_n$ plot for St polymerization initiated with CPTPV at 110 ℃: [CPTPV] = 6 (●), 12 (△), and 24 mmol/L (○).

shown in Fig. 3, $\overline{M}_w/\overline{M}_n$ was not reduced to below 1.5 in the concentration range of CPTPV examined. The results given by Figs. 1, 2, and 3 indicate that CPTPV cannot mediate the pure "living" free radical polymerization under these conditions.

The presence of the cyanopropyl group and TPV moiety at the termini of the PSt was confirmed by ^{1}H-NMR spectroscopy as summarized in Table 1. Although the content of the cyanopropyl end group and $\overline{M}_n$ at low conversions were found to increase and decrease with increasing CPTPV concentration, simultaneously, the cyanopropyl group was not introduced quantitatively. If all the propagating radicals participated exclusively in the bimolecular termination by combination, no TPV can be bound as the end group. The TPV content remained almost constant at ca. 40% irrespective of the content of the cyanopropyl group indicating that ca. 60% of the polymer ω-ends were formed by the ordinary bimolecular termination.

Table 1. End groups from CPTPV bound to PSt prepared at 110 ℃

[CPTPV] (mmol/L)	Time (h)	Convn. (%)	$\overline{M}_n$ a)	$\overline{M}_w/\overline{M}_n$ a)	Content of end group$^{b)}$ (%)	
					Cyanopropyl	TPV
6	2	6.6	20600	3.69	44	38
12	2	3.5	9600	2.88	60	37
24	2	3.2	6000	1.87	68	40

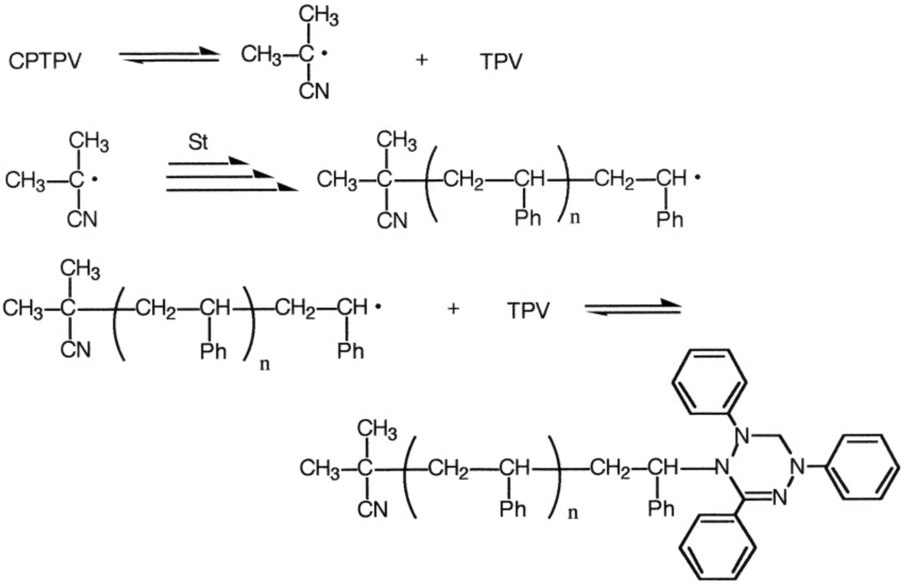
a) Determined by GPC. b) Determined by ^{1}H-NMR spectroscopy.

Thermal dissociation of CPTPV has been shown to regenerate TPV at 40 °C or above (10), and the coupling product of TPV with the PSt radical is dissociable at 110 °C as can be seen from the increase in $\overline{M}_n$ with conversion as shown in Fig. 2. The polymerization was carried out at different temperatures to change the extent of the dissociation of the C-N bond at the polymer chain end. The polymerizations at 90, 100, and 120 °C using 12 mmol/L of CPTPV were found to fit to first order kinetic plots as well as the polymerization at 110 °C. Furthermore, the rates of the polymerization are quite similar to the thermal polymerization rates at respective temperatures. Almost the same dependence of $\overline{M}_n$ on conversion with that shown in Fig. 2 was observed irrespective of temperature; the number of polymer chain from the same concentration of CPTPV remained constant. Apparently, the dissociation of CPTPV and initiation by the cyanopropyl radical are sufficiently fast at 110 °C.

However, experimentally determined $\overline{M}_n$, which, exceeded the theoretical $\overline{M}_n$ up to 50% conversion, decreased with increasing conversion at higher conversion range particularly at 120 °C. The ordinary bimolecular termination, which is involved in conventional radical polymerization, may result in a decrease in the number of the polymer chain bearing the dissociable C-N and the higher $\overline{M}_n$ at the low conversion range. After polymerization for a longer period at 120 °C, a significant amount of the active propagating radicals would irreversibly terminate and the further increase in $\overline{M}_n$ could not be expected. The values of $\overline{M}_w/\overline{M}_n$ of the PSt at different temperatures were not reduced to below 1.8, and a considerable contribution of the ordinary bimolecular termination was confirmed at

120 °C as well as at 90 °C.

Therefore, CPTPV can initiate the St polymerization and the PSt-TPV can also dissociate into the active PSt radical and TPV as shown in Scheme 1. One of the possible reasons for the uncontrolled polymerization seems to be the decomposition of TPV (15) which would result in an excess amount of the cyanopropyl radical or PSt radical. The coupling of TPV at a reduced concentration with the active propagating radical cannot be sufficiently fast, and the conventional bimolecular termination could significantly contribute as end forming reaction.



Scheme 1

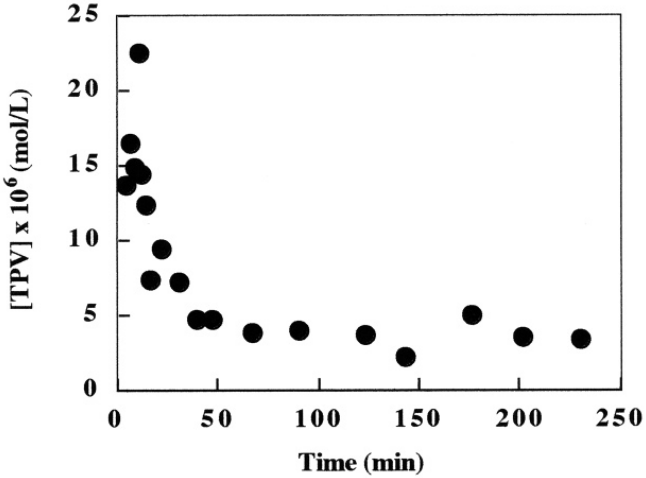


Fig. 4. Change in TPV concentration monitored by ESR spectroscopy during CPTPV initiated St polymerization at 110 °C: [CPTPV] = 12 mmol/L

Fig. 4 shows the change in TPV concentration monitored by ESR spectroscopy during the polymerization at 110 °C. Apparently, the concentration of TPV increases first by the rapid dissociation of CPTPV followed by decomposition of TPV to non-radical product. Although the decomposition rate of TPV at 110 °C is not known, the decrease in the TPV concentration primarily by the decomposition may result in the slower scavenge of the propagating radical with TPV thus allowing bimolecular termination. The TPV concentration seems to settle at ca. 3.6 x 10^{-6} mol/L. It should be reminded that the TEMPO concentration in the living radical polymerization of St has been estimated to be of the order of 10^{-5} mol/L (14).

In conclusion, the coupling product of TPV can dissociate into TPV and the 2-cyano-2-propyl radical which initiates the St polymerization. Although the $\overline{M}_n$ of the PSt increased with conversion as well as that of the PSt obtained by the living radical polymerization, the sufficiently high concentration of TPV cannot be maintained due to the thermal decomposition of TPV. If a structurally modified TPV is sufficiently stable at polymerization temperature, such a radical could be the mediator for the “living” free radical polymerization.

References

1. Recent review, Colombani D (1997) Prog Polym Sci 22: 1649
2. Yamada B, Miura Y, Nobukane Y, Aota M (1997) In: Matyjaszewski K (ed) Controlled Radical Polymerization. American Chemical Society, Washington (ACS Symposium Series 685, Chap 12)
3. Shigemoto T, Matyjaszewski K (1996) Macromol Chem Rapid Commun 17: 347
4. Colombani D, Steenbock M, Klapper M, Müllen K (1997) Macroml Chem Rapid Commun 18: 243
5. Steenbock M, Mapper M, Müllen K (1998) Macroml Chem Phys 199: 761
6. Kuhn R, Trishcmann H (1964) Monatsh Chem 95: 457
7. Otsu T, Yamada B, Ishikawa T (1991) Macromolecules 24: 415
8. Yamada B, Yoshikawa E, Shiraishi K, Miura H, Otsu T (1991) Polymer 32: 1892
9. Yamada B, Kageoka M, Otsu T (1991) Macromolecules 24: 5234
10. Neugebauer FA (1966) Monatsh Chem 97: 853
11. Kinoshita M, Miura Y (1969) Makromol Chem 124: 211
12. Yamada B, Tanaka H, Konishi K, Otsu T (1994) J Macromol Sci Pure Appl Chem A31: 351
13. Meister BJ, Malanga, MT (1989) In: Mark HF, Bikales NM, Overberger CG, Menges G, Kroshnitz JK (ed) Encyclopedia of Polymer Science and Engineering. Wiley, New York (vol 16, p 13)
14. Fukuda T, Terauchi A, Goto A, Ohno K, Tsujii Y, Miyamoto T, Kobatake S, Yamada B (1996) Macromolecules 29: 6393
15. Neugebauer FA, Otting W, Smith HO, Trishmann H (1972) Chem Ber 105: 549