Eur. Polym. J. Vol. 24, No. 2, pp. 129–136, 1988
Printed in Great Britain

0014-3057/88 \$3.00 + 0.00
Pergamon Journals Ltd

POSTPOLYMERIZATION AND BLOCK COPOLYMERIZATION BY USING LONG-LIVED POLY(*N*-METHYLMETHACRYLAMIDE) RADICALS

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(*Received* 31 *March* 1987)

Abstract—The photopolymerization of *N*-methylmethacrylamide (NMMAm) with di-tert-butyl peroxide in cyclohexane produced long-lived poly(NMMAm) radicals in the polymerization system. The postpolymerization was attempted by using the long-lived poly(NMMAm) radicals. The postpolymerization occurred to a greater extent as the monomer concentration, the temperature and the conversion of prepolymerization were higher. GPC and viscometric results revealed that the molecular weight and its distribution for the resulting poly(NMMAm) were increased by the postpolymerization. The long-lived poly(NMMAm) radicals were found by ESR to react gradually with vinyl monomers at room temperature to yield the stable propagating radicals of the second monomer. Block copolymer was prepared by the reaction of poly(NMAAm) radicals with methyl acrylate (MA). The MA conversion increased with increasing MA concentration. The MA conversion increased with time up to about 100% in the reaction for 45 hr. The block copolymer constituted 42–76% of the total polymer. The MA conversion showed a maximum at 35°C with varying temperature, while the block efficiency decreased with increasing temperature. The reactions of poly(NMMAm) radicals with some other vinyl monomers were also examined.

INTRODUCTION

N-Methacrylamide and *N*-methylmethacrylamide-(NMMAm) are polymerized by radical initiators in benzene to give polymer microspheres. The microspheres contain many long-lived propagating radicals of these amide monomers [1–4]. The long-lived polymer radicals react easily with other vinyl monomers such as styrene (St) and methyl methacrylate (MMA) at room temperature to yield stable propagating radicals of the second monomers [4].

As reported previously, when NMMAm is polymerized by radical initiators in cyclohexane which has a slight affinity for the NMMAm monomer, in contrast to benzene, the resulting polymer is precipitated as coral-like conglomerates [5]. The conglomerates also contain a number of long-lived propagating radicals of NMMAm.

The present paper deals with the postpolymerization and block copolymerization by using long-lived poly(NMMAm) radicals in cyclohexane.

The following abbreviations are used; methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (BA), cyclohexyl methacrylate (CyMA), benzyl methacylate (BzMA), acrylonitrile(AN), vinyl acetate (VAc), di-tert-butyl peroxide (DBPO), methanol (MeOH) and ethyl acetate(EtOAc).

EXPERIMENTAL

NMMAm was prepared by the reaction of methylamine with methacryloyl chloride [5]. DBPO as photoinitiator was purified by distillation at reduced pressure. Monomers and solvents were used after distillations.

The polymerization was carried out in a degassed sealed tube at a constant temperature. The photopolymerization of NMMAm with DBPO was performed at 30°C by using a merry-go-round type apparatus with a 400W high-pressure Mg lamp. Then the polymerization mixture was heated to give postpolymerization without irradiation. The resulting poly(NMMAm) was isolated by pouring the polymerization mixture into a large excess of EtOAc. Intrinsic viscosity ($[\eta]$) of poly(NMAAm) was measured at 30°C in MeOH by an Ubbelohde viscometer.

The block copolymerization was accomplished thus: a cyclohexane solution (2 ml) of NMMAm (3.03 mol/l) and DBPO (2.71×10^{-2} mol/l) was charged in a glass tube with a rubber stopper and with a connection to a vacuum system. After being degassed, the contents were irradiated for 15 hr at 40°C to yield the living poly(NMMAm) radicals. In this step, NMMAm was separately confirmed to be photopolymerized to a 97% yield. To this reaction mixture, a second monomer (2 ml) was added with a syringe in a N_2 atmosphere through the rubber cap. The system was then degassed and sealed under vacuum. The poly(NMMAm) radicals were allowed to react with the second monomer at a definite temperature without shaking. After a given time, the reaction mixture was poured into a large amount of ether. Precipitated polymer was isolated by filtration, dried under vacuum and subjected to fractionation. The isolated polymer mixture was fractionated into three parts by Soxhlet extraction which was carried out for 15 hr. EtOAc was first used as extracting solvent for the homopolymer of the second monomer. Second, homopoly(NMMAm) was extracted by MeOH. The insoluble residue was taken as block copolymer.

ESR spectra of the polymerization mixtures in a degassed sealed ESR tube were recorded by using a JEOL-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity.

Gel permeation chromatograms (GPC) were recorded at 40°C using a combination system of pump (Trirotar-V, Japan spectroscopic Co., Ltd), RI detector (SE-31, Shodex) and two columns (TSK gel G6000Pw + G3000Pw), where a phosphate buffer solution (pH 8) was used as carrier. From

GPC results, the number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights were determined by standard procedures, in which polyethylene-glycols were used for calibration.

Dynamic thermogravimetry (TG) of the resulting polymers was performed in a N_2 atmosphere (flow rate 20 ml/min) with a thermogravimeter (Shimadzu TG-30) at a heating rate of 10°C/min. All runs were terminated at 500°C.

RESULTS AND DISCUSSION

Photopolymerization of NMMAm with DBPO in cyclohexane

The photopolymerization of NMMAm with DBPO was examined in cyclohexane at 30°C. Figure 1 shows the dependence of polymerization rate (R_p) on DBPO concentration, where the NMMAm concentration was kept at 3.37 mol/l. R_p was found to be proportional to (initiator concentration).$^{0.12}$ Thus R_p was little dependent on the DBPO concentration. NMMAm also was appreciably polymerized in the absence of DBPO. These findings indicate that the NMMAm monomer itself acted as photo-sensitizer.

Since long-lived poly(NMMAm) radicals are formed in the polymerization of NMMAm with azobisisobutyronitrile in cyclohexane [5], we have also investigated the photopolymerization with DBPO in cyclohexane by means of ESR.

Figure 2 shows ESR spectral changes with time for the photopolymerization at 22°C, where the concentrations of NMMAm and DBPO were 3.37 and 2.71×10^{-2} mol/l, respectively. Thus, the five-line spectrum due to the propagating poly(NMMAm) radicals increased in intensity with time.

Figure 3 shows a plot of the polymer radical concentration against the polymerization time. The long-lived polymer radicals increased in concentration in proportion to the irradiation time. Thus the long-lived poly(NMMAm) radicals were found to be readily produced in the photopolymerization system also.

Next, the stability of polymer radicals was examined. Figure 4 shows the change of the polymer radical concentration with time at 22° and 60°C after photopolymerization for 1 hr at 22°C. At 22°C, the polymer radical concentration slowly fell with time and about 80% of the radicals were stable after 18 hr. At 60°C, the polymer radical concentration decreased at a fairly high rate for about 4 hr and then showed little decrease. After about 5 hr, half of the radicals were still alive. These results indicate that a definite portion of the poly(NMMAm) radicals survived as such under the present conditions.

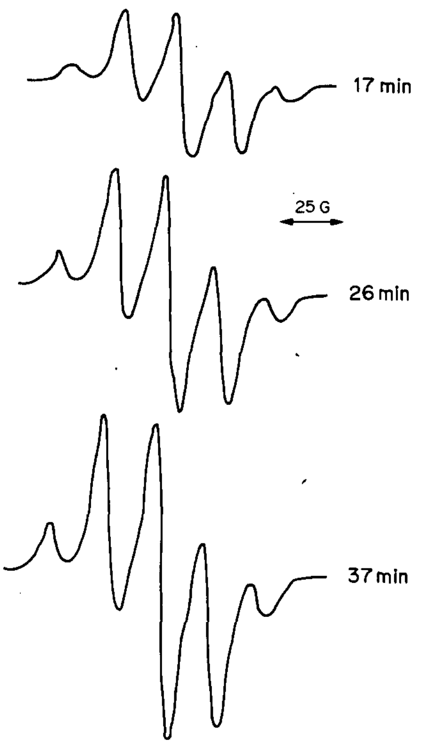


Fig. 2. ESR spectral change of the polymerization mixture with irradiation time at 22°C; [NMMAm] = 3.37 mol/l, [DBPO] = 2.71×10^{-2} mol/l.

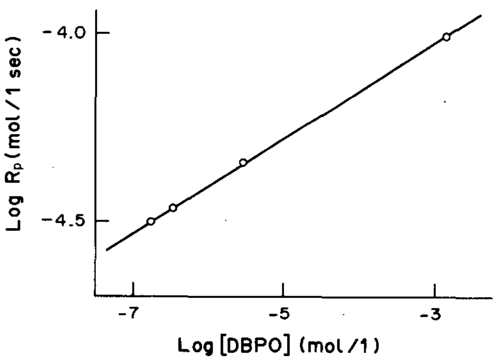


Fig. 1. Relationship between the DBPO concentration and the photopolymerization rate (R_p) at 30°C in cyclohexane; [NMMAm] = 3.37 mol/l.

Postpolymerization after the photopolymerization of NMMAm with DBPO in cyclohexane

As mentioned above, it is clear that long-lived poly(NMMAm) radicals were also produced in this

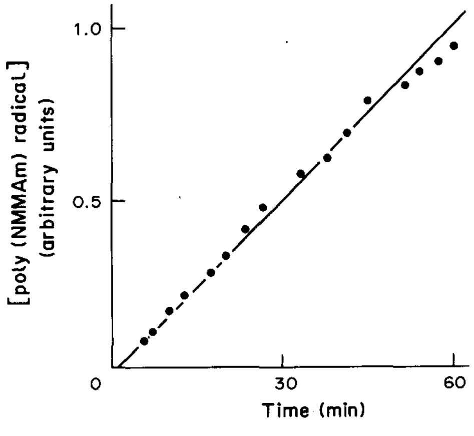


Fig. 3. Relationship between time and the poly(NMMAm) radical concentration in the photopolymerization of NMMAm with DBPO at 22°C in cyclohexane; [NMMAm] = 3.37 mol/l, [DBPO] = 2.71×10^{-2} mol/l.

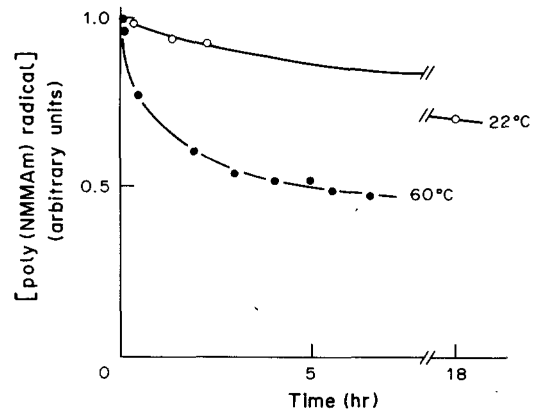


Fig. 4. Change of the polymer radical concentration with time at 22°C and 60°C after the photopolymerization of NMMAm with DBPO for 1 hr at 22°C; [NMMAm] = 3.37 mol/l, [DBPO] = 2.71×10^{-2} mol/l.

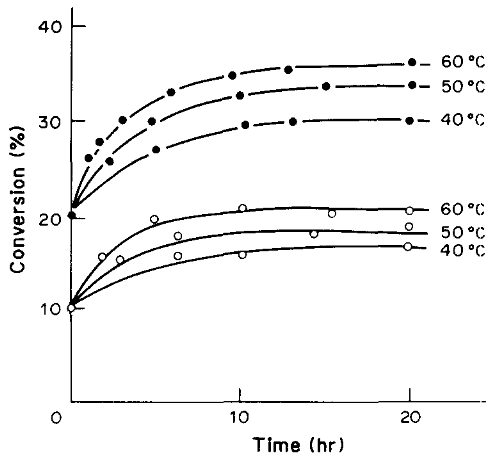


Fig. 5. Time–conversion curves observed in the postpolymerization; a cyclohexane solution of NMMAm (3.37 mol/l) and DBPO (2.71×10^{-2} mol/l) was irradiated at 30°C and then heated to be postpolymerized.

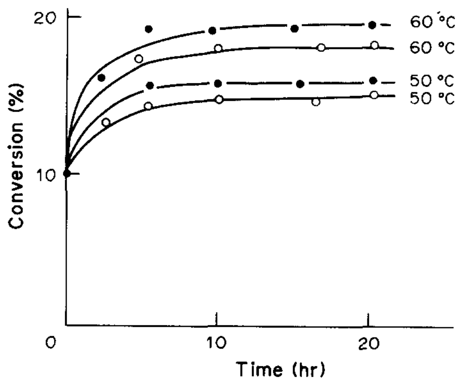


Fig. 6. Effect of the monomer concentration on the postpolymerization; [NMMAm] = 3.37 (○) and 6.06 (●) mol/l. A cyclohexane solution of NMMAm and DBPO (2.71×10^{-2} mol/l) was irradiated at 30°C and then heated to be postpolymerized.

system. So, the postpolymerization was attempted by using this polymerization system.

NMMAm was previously photopolymerized with DBPO in cyclohexane up to conversions of 10% and 20%. Then the resulting polymerization mixture was allowed to react further at a given temperature without irradiation. The thermal polymerization of NMMAm with DBPO at 60°C was separately confirmed to proceed slightly.

Figure 5 shows the time–conversion curves observed in the postpolymerization at 40°, 50° and 60°C. The conversion during postpolymerization increased as the temperature and the conversion of prepolymerization were higher. The polymer radicals were more mobile at higher temperatures, leading to easy reaction with unreacted monomers. As the prepolymerization conversion increased, more long-lived polymer radicals were generated. After about 10 hr, the conversion became almost constant. These results conform to those shown in Fig. 4.

As can be seen from Fig. 6, the postpolymerization proceeded more as the monomer concentration was higher. Cyclohexane has little affinity for poly(NMMAm), while NMMAm has an appreciable affinity for the polymer. Therefore, the higher monomer concentration gives the polymer radicals a higher mobility, and so a higher reactivity.

From these results, it was expected that the NMMAm polymer chain was elongated by the postpolymerization. So, in order to obtain information on the molecular weight of resulting poly(NMMAm), the intrinsic viscosities ([η]) of the polymers were measured in methanol.

Table 1 shows [η] of poly(NMMAm) before and after the postpolymerization. In all cases, the molecular weight was increased by the postpolymerization.

Table 2 summarizes the molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) determined by GPC. In both cases of 10% and

Table 1. Effect of the postpolymerization on the intrinsic viscosity ([η]) of the resulting poly(NMMAm)

[NMMAm] (mol/l)	Conversion in prepolymerization* (%)	Temperature of postpolymerization (°C)	Time of postpolymerization (hr)	Conversion in postpolymerization (%)	[η]† (dl/g)
3.37	10	—	0	0	0.15
3.37	10	40	20	5	0.20
3.37	10	50	20	8	0.21
3.37	10	60	20	11	0.23
3.37	20	—	0	0	0.21
3.37	20	50	20	13	0.25
6.06	10	—	0	0	0.19
6.06	10	50	20	10	0.28

*A cyclohexane solution of NMMAm and DBPO (2.71×10^{-2} mol/l) was irradiated at 30°C.
†Measured in MeOH at 30°C.

Table 2. The molecular weights ($\overline{M}_n$ and $\overline{M}_w$) of poly(NMMAm) and the molecular weight distribution ($\overline{M}_w/\overline{M}_n$) by GPC

Conversion in prepolymerization* (%)	Time of postpolymerization (hr)	Conv. in postpolymerization (%)	$\overline{M}_n$ ($\times 10^{-4}$)	$\overline{M}_w$ ($\times 10^{-5}$)	$\overline{M}_w/\overline{M}_n$
10	0	0	5.8	1.06	1.87
10	18	8	5.9	2.06	3.47
20	0	0	5.1	1.41	2.76
20	2.5	5	5.2	1.63	3.15
20	15	13	5.7	2.28	4.00

*A cyclohexane solution of NMMAm (3.37 mol/l) and DBPO (2.71×10^{-2} mol/l) was irradiated at 30°C; postpolymerization was carried out at 50°C.

20% of prepolymerization, the molecular weight of poly(NMMAm) increased after postpolymerization. Further the molecular weight distribution was broadened, indicating that only the long-lived poly(NMMAm) radicals near the surfaces of the polymer particle, which were more mobile, reacted with the unreacted monomer.

ESR study on the reaction of long-lived poly(NMMAm) radicals with vinyl monomers

As mentioned above, the long-lived poly(NMMAm) radicals were produced by the radical polymerization of NMMAm in cyclohexane and undergo postpolymerization. Next, the reaction of the polymer radicals with some vinyl monomers was investigated by ESR. The monomers used were AN, MMA and St.

Figure 7 shows ESR spectral change with time for the reaction of poly(NMMAm) radicals with AN at room temperature. The five-line spectrum due to poly(NMMAm) radicals was gradually converted into a three-line spectrum and then the triplet spectrum changed to a broad singlet. A similar three-line spectrum was reported to be observed on γ-ray irradiation of AN at low temperature, where oligomers are considered to be formed [6], while the occluded polymer radicals formed in the usual poly-

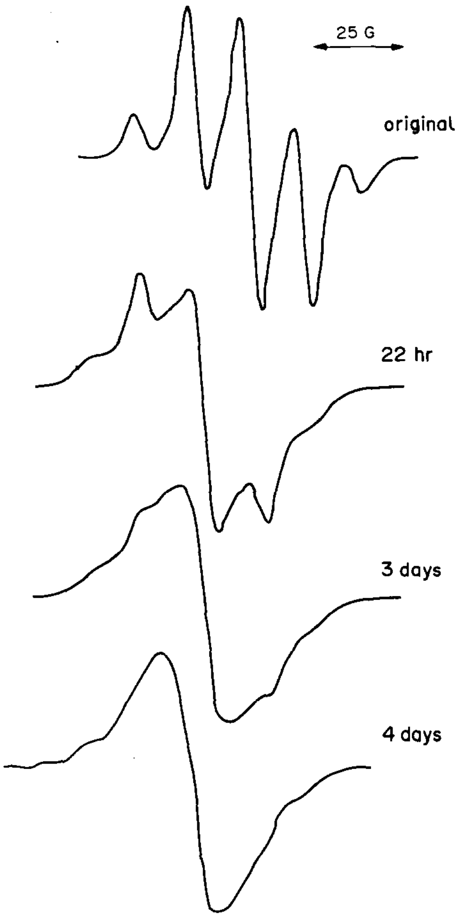


Fig. 7. ESR spectral change of the poly(NMMAm) radical/AN system; a cyclohexane solution (0.08 ml) of NMMAm (3.03 mol/l) and DBPO (2.71×10^{-2} mol/l) was irradiated for 2 hr at room temperature and then 0.2 ml of AN was added.

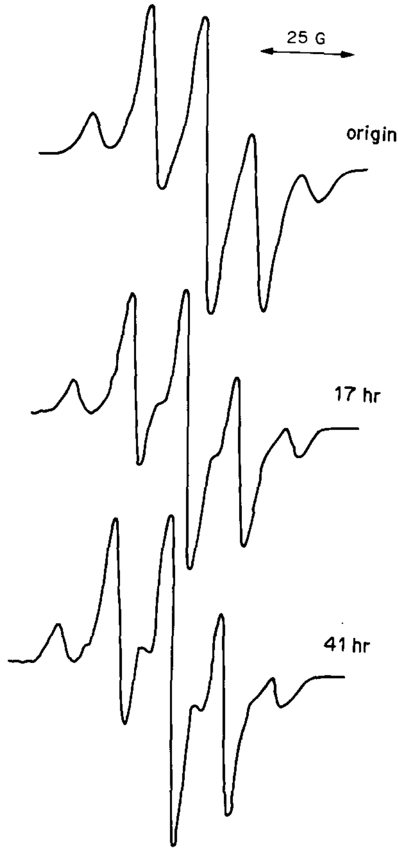
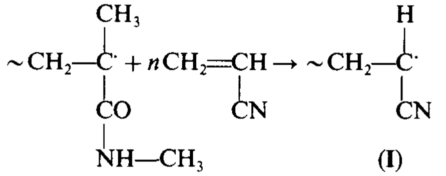


Fig. 8. ESR spectral change of the poly(NMMAm) radical/MMA system; a cyclohexane solution (0.08 ml) of NMMAm (3.03 mol/l) and DBPO (2.71×10^{-2} mol/l) was irradiated for 2 hr at room temperature and then 0.2 ml of MMA was added.

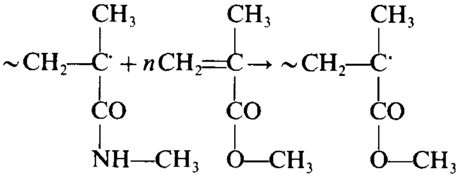
merization of AN shows a broad singlet [7]. The change in the spectrum of the reaction mixture seems to originate from the change in the environment around the radical centres of poly(AN) radicals, depending on the number of AN monomeric units incorporated in the polymer radicals. Thus long-lived poly(NMMAm) radicals was found to react easily with AN at room temperature, giving long-lived poly(AN) radicals(**I**) [eqn (1)].



$$\sim CH_2-\overset{CH_3}{\underset{CO-NH-CH_3}{C^{\cdot}}} + n\,CH_2{=}\underset{CN}{CH} \rightarrow \sim CH_2-\overset{H}{\underset{CN}{C^{\cdot}}} \qquad (1)$$

(**I**)

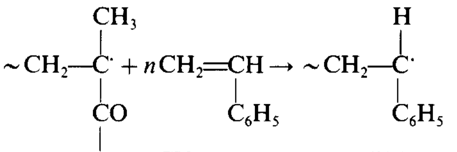
As shown in Fig. 8, when MMA was used as second monomer, the five-line spectrum due to poly(NMMAm) radicals was changed to a nine-line spectrum. This nine-line spectrum was assignable to poly(MMA) radical [8, 9]. This indicates that poly(NMMAm) radicals reacted with MMA to yield stable poly(MMA) radicals(**II**) [eqn (2)].



$$\sim CH_2-\overset{CH_3}{\underset{CO-NH-CH_3}{C^{\cdot}}} + n\,CH_2{=}\overset{CH_3}{\underset{CO-O-CH_3}{C}} \rightarrow \sim CH_2-\overset{CH_3}{\underset{CO-O-CH_3}{C^{\cdot}}} \qquad (2)$$

(**II**)

Figure 9 shows ESR spectral changes when St was second monomer. The five-line spectrum was changed to the three-line spectrum of propagating poly(St) radicals(**III**) [10]. St also reacted easily with poly(NMMAm) radicals to give long-lived poly(St) radicals [eqn (3)].



$$\sim CH_2-\overset{CH_3}{\underset{CO-NH-CH_3}{C^{\cdot}}} + n\,CH_2{=}\underset{C_6H_5}{CH} \rightarrow \sim CH_2-\overset{H}{\underset{C_6H_5}{C^{\cdot}}} \qquad (3)$$

(**III**)

These results show that long-lived poly(NMMAm) radicals react with second monomers at room temperature and produce the stable propagating radicals of the second monomers.

Synthesis of block copolymers by the reaction of long-lived poly(NMMAm) radicals with vinyl monomers

The photopolymerization of NMMAm with DBPO in cyclohexane proceeded almost quantitatively (97% yield). The resulting polymerization mixture contained long-lived poly(NMMAm) radicals which reacted readily with vinyl monomers to yield long-lived propagating radicals of the second monomers. Therefore, this reaction system was applied to synthesis of block copolymers.

The block copolymerization through the reaction of poly(NMMAm) radicals with MA was mainly examined. Figure 10 shows the relationship between the MA concentration and the MA conversion in the reaction of poly(NMMAm) radicals with MA at 40°C for 26 hr, where benzene was used as diluent. The MA conversion tended to increase with increasing MA concentration.

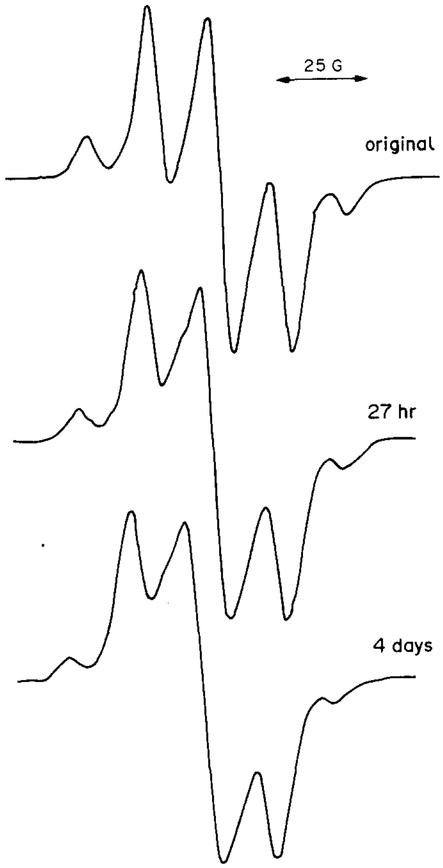


Fig. 9. ESR spectral change of the poly(NMMAm) radical/St system; a cyclohexane solution (0.08 ml) of NMMAm (3.03 mol/l) and DBPO (2.71 × 10^{-2} mol/l) was irradiated for 2 hr at room temperature and then 0.2 ml of St was added.

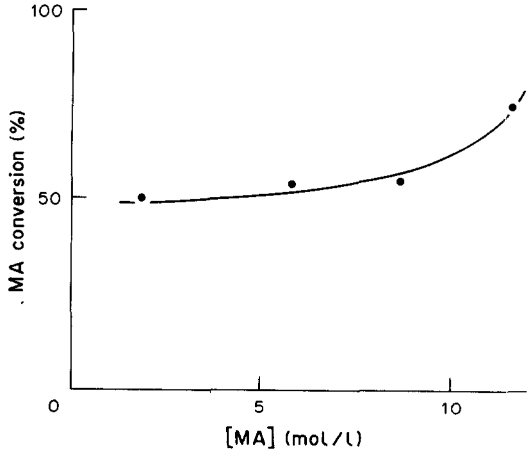


Fig. 10. Relationship between the MA concentration and the MA conversion in the reaction of poly(NMMAm) radicals with MA for 26 hr at 40°C; a cyclohexane solution (2 ml) of NMMAm (3.03 mol/l) and DBPO (2.71 × 10^{-2}) was irradiated for 15 hr at 40°C and then a benzene solution (2 ml) of MA was added.

Table 3. Effect of MA concentration on the reaction of poly(NMMAm) radicals* with MA at 40°C for 26 hr

Run	[MA]† (mol/l)	Conversion of MA (%)	Fraction (wt%) EtOAc-soluble	MeOH-soluble	Insoluble
1	2.90	50	10	40	50
2	5.81	54	19	39	52
3	8.71	55	14	38	48
4	11.60	76	11	26	63

*A cyclohexane solution (2 ml) of NMMAm (3.03 mol/l) and DBPO (2.71×10^{-2} mol/l) was irradiated at 48°C for 15 hr.

†The MA concentration of the benzene solution (2 ml) added to the polymer radical mixture.

Table 3 summarizes the results of fractionation of the polymer mixture formed. The fraction of block copolymer (insoluble in both MeOH and EtOAc) was in the range from 42% to 63%. A considerable portion (26–40%) of the polymer was extracted with MeOH, suggesting that minor amounts of long-lived poly(NMMAm) radicals participated in the block copolymerization. The MA monomer might with difficulty under the present conditions diffuse to the radical centres. However, it should be noted that the MeOH solution obtained by Sohxlet extraction showed a milky turbidity on cooling at room temperature. Further, as described below, the i.r. spectrum of the MeOH-soluble part showed an absorption band at 1750 cm^{-1} due to ester carbonyl group. These findings indicate that the MeOH-soluble part contained block copolymer carrying short chains of poly(MA).

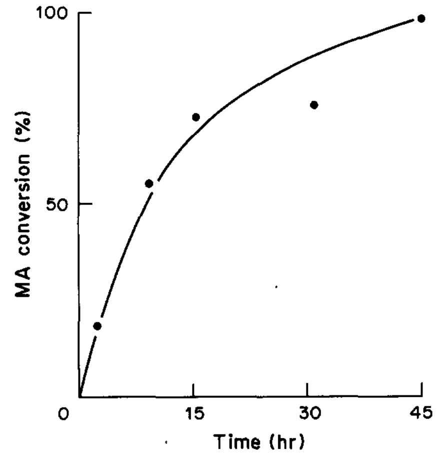


Fig. 11. Relationship between time and MA conversion in the reaction of poly(NMMAm) radicals with MA at 40°C; a cyclohexane solution (2 ml) of NMMAm (3.03 mol/l) and DBPO (2.71×10^{-2} mol/l) was irradiated for 15 hr at 40°C and then 2 ml of MA was added.

Figure 11 shows the effect of reaction time on the MA conversion when poly(NMMAm) radicals were allowed to react with neat MA at 40°C. The MA conversion increased with time up to about 100% during reaction for 45 hr. Table 4 presents the results of fractionation. The fraction of block copolymer constituted 55–76% of the total polymer, and showed a trend to decrease with time. The propagating polymer radicals might find more chances of chain transfer at longer reaction time.

Figure 12 shows the temperature effect on the MA conversion in the reaction of poly(NMMAm) radicals with neat MA for 8.5 hr. The MA conversion showed a maximum at 35°C. This is because poly(NMMAm) radicals were more easily deactivated by bimolecular termination or chain transfer at higher temperatures. Table 5 shows the results of fractionation. The insoluble fraction decreased with temperature, indicating that chain transfer reactions of the

Table 4. Effect of the reaction time on the reaction of poly(NMMAm) radicals* with MA† at 40°C

Run	Time (hr)	Conversion of MA (%)	Fraction (wt%) EtOAc-soluble	MeOH-soluble	Insoluble
5	4.0	18	4	20	76
6	8.5	56	12	22	66
7	15.0	74	10	22	68
8	31.0	76	29	15	56
9	45.0	100*ca*	14	23	63

*A cyclohexane solution (2 ml) of NMMAm (3.03 mol/) and DBPO (2.71×10^{-2} mol/l) was irradiated at 40°C for 15 hr.

†The neat MA (2 ml) was added to the polymer radical mixture.

Table 5. Temperature effect on the reaction of poly(NMMAm) radicals* with MA† for 8.5 hr

Run	Temperature (°C)	Conversion of MA (%)	Fraction (wt%) EtOAc-soluble	MeOH-soluble	Insoluble
10	20	64	5	17	78
11	30	72	3	23	74
12	35	81	10	24	66
13	40	61	12	24	64
14	50	54	29	37	34
15	60	11	14	50	36

*A cyclohexane solution (2 ml) of NMMAm (3.03 mol/l) and DBPO (2.71×10^{-2} mol/l) was irradiated at 40°C for 15 hr.

†The neat MA(2 ml) was added to the polymer radical mixture.

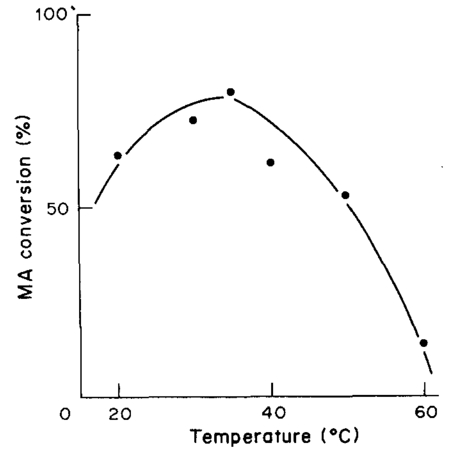


Fig. 12. Temperature effect on MA conversion in the reaction of poly(NMMAm) radicals with MA for 8.5 hr; a cyclohexane solution (2 ml) of NMMAm (3.03 mol/l) and DBPO (2.71 × 10^{-2} mol/l) was irradiated for 15 hr at 40°C and then 2 ml of MA was added.

propagating radicals were more pronounced at higher temperatures.

Table 6 lists the results of the reaction of poly(NMMAm) radicals with other monomers at 40°C for 8.5 hr.

EA was polymerized to 70% yield. The block efficiency in the EA system was also high. However, BA showed very low polymer yield. The large alkyl group of BA might prevent access of the monomer to the polymer radical centres.

A similar tendency was observed in the reaction of methacrylate monomers. MMA was polymerized in a fairly high yield of 53%. But BzMA and CyMA showed low conversions.

St gave a low polymer yield although the monomer was confirmed by the ESR study to react readily with poly(NMMAm) radicals. The propagation of poly(St) radicals might be very slow under the present conditions.

AN showed relatively high conversions and block yields. High affinity of AN for poly(NMMAm) caused easy access of the monomer to the active centres. Separation of homopoly(AN) from the block copolymer was not carried out because a suitable extracting solvent could not be found. This might contribute in part to the high block yield. However, AN is known to be scarcely polymerized during thermal polymerization without initiator.

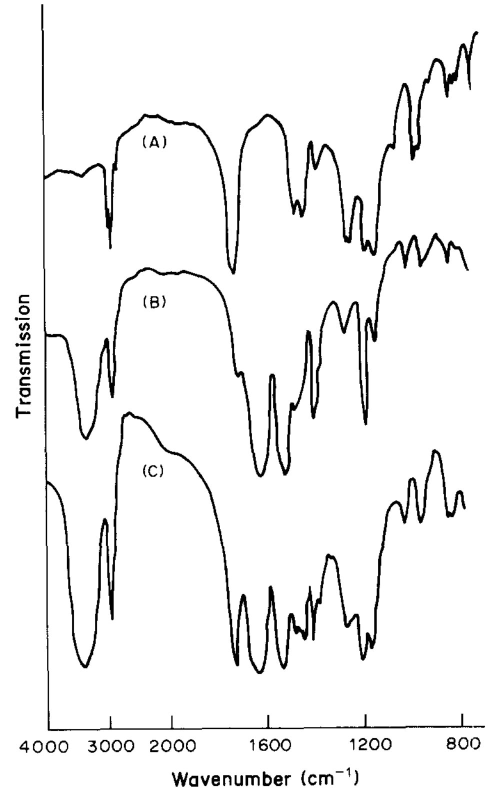


Fig. 13. i.r. Spectra of the AcOEt-soluble (A), MeOH-soluble (B) and insoluble (C) parts obtained in the reaction of poly(NMMAm) radicals with MA (Run 13).

VAc also gave low conversion. The non-conjugative monomer is considered to have only a slight reactivity toward poly(NMMAm) radicals [11].

Characterization of block copolymers

Figure 13 presents i.r. spectra of fractionated polymers obtained in the reaction of poly(NMMAm) radicals with MA as second monomer. The spectrum of the EtOAc-soluble part(A) was almost identical with that of poly(MA), indicating that this part was homopoly(MA). The MeOH-soluble part(B) showed slight absorption at 1750 cm^{-1} due to the ester group together with those (1650, 1550 cm^{-1}) due to amide

Table 6. Reaction of poly(NMMAm) radicals* with some vinyl monomers† at 40°C for 8.5 hr

Run	Second monomer	Conversion of MA (%)	Fraction (wt%)		
			EtOAc-soluble	MeOH-soluble	Insoluble
13	MA	61	12	24	64
16	EA	73	4	10	86
17	BA	1	19	80	1
18	MMA	53	4	46	50
19	BzMA	5	5	87	8
20	CyMA	8	6	72	22
21	St	6	13	81	6
22	AN	38	—	55	45
23	VAc	4	1	98	1

*A cyclohexane solution (2 ml) of NMMAm (3.03 mol/l) and DBPO (2.71 × 10^{-2} mol/l) was irradiated at 40°C for 15 hr.

†The neat second monomer (2 ml) was added to the polymer radical mixture.

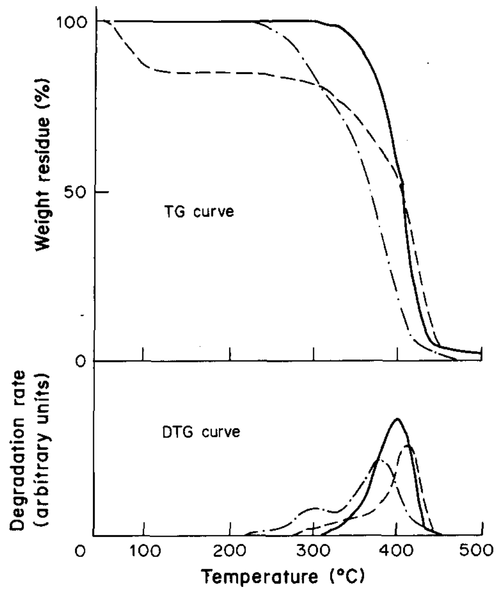


Fig. 14. TG and DTG curves of the block copolymer obtained in the reaction of poly(NMMAm) radicals with MA (Run 13) (——), poly(MA) (—·—) and poly(NMMAm) (-----).

group. This reveals that the MeOH-soluble part consisted of homopoly(NMMAm) and block copolymer bearing short chains of poly(MA). The solvent-insoluble part(C) exhibited absorption bands due to both carbonyl groups of the ester and amide. Thus, the insoluble part was reasonably taken as block copolymer.

Similar i.r. spectroscopic results were observed for the fractions obtained from the reaction of poly(NMMAm) radicals with MMA.

Thermal degradation of the block copolymer from MA was studied thermogravimetrically. TG and differential thermogravimetric (DTG) curves of the block copolymer are shown in Fig. 14 together with those for poly(MA) and poly(NMMAm) separately prepared. Thus the degradation behaviour of block copolymer was different from those of the homopolymers. The maximum degradation temperature of block copolymer was observed between those of the homopolymers.

Acknowledgements—The authors are grateful to Mr M. Tanaka (Tokushima University of Arts and Science) for GPC measurement. They are also indebted to the Mazda Foundation for the partial support of this research.

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