Long-lived polymer radicals: 5. Synthesis of block copolymer by the reaction of living poly(*N*-phenylmethacrylamide) radical with vinyl monomers

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When *N*-phenylmethacrylamide (NPMAm) was photopolymerized at room temperature in benzene by using di-*tert*-butyl peroxide as sensitizer, the resulting heterogeneous polymerization mixture was found to contain very stable propagating poly(NPMAm) radical. An e.s.r. study revealed that the living polymer radical reacted easily at room temperature with methyl methacrylate (MMA) yielding persistent poly(MMA) radical. Block copolymer was prepared by the reaction of living poly(NPMAm) radical with MMA and methyl acrylate. Block copolymer constituted 30–60% of the resultant total polymer. Block copolymer was characterized by g.p.c., i.r. spectroscopy and electron microscopy.

Keywords *N*-Phenylmethacrylamide; living polymer radical; block copolymer; e.s.r. spectrum

INTRODUCTION

N-Methylacrylamide and *N*-methylmethacrylamide were reported to produce the living propagating polymer radicals, when the amide monomers were polymerized by using radical initiator in adequate solvents such as benzene, carbon tetrachloride and dioxane[1]. The living polymer radicals were found to react easily at room temperature with various vinyl monomers to yield the propagating radicals of the second monomers, which were stable enough to be subjected to e.s.r. measurement[2]. Further, some block copolymers were prepared by the reactions of the living polymer radicals of the amide monomers with vinyl monomers[1,3,4].

Recently, we have found that *N*-phenylmethacrylamide (NPMAm), an amide monomer, also yielded the stable propagating polymer radical on radical polymerization in benzene.

The present paper describes a synthesis of block copolymer via the reaction of living poly(NPMAm) radical with vinyl monomers.

EXPERIMENTAL

NPMAm was prepared by the reaction of methacryloyl chloride with aniline in acetonitrile and recrystallized from toluene (m.p. 88°C). Other monomers, initiators and solvents were used after usual purifications.

Homopolymerization of NPMAm by using azo-bis-isobutyronitrile (AIBN) or di-*tert*-butyl peroxide (DBPO) as photosensitizer was carried out in a degassed and sealed glass tube. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of ether.

Block copolymerization was performed in the following manner. A solution of NPMAm and DBPO in benzene 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 5 h at room temperature by using a high-pressure mercury lamp (100 W) to yield the living poly(NPMAm) radical. To this reaction mixture, a second monomer was added with a syringe in a nitrogen atmosphere through the rubber cap. The system was then degassed and sealed under a vacuum. The reaction of poly(NPMAm) radical with the second monomer was allowed 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. Unreacted NPMAm monomer was recovered by evaporation of the solvent from the filtrate. The isolated polymer mixture was divided into three parts by fractional precipitation.

The reaction of MMA with the living poly(NPMAm) radical formed in a degassed e.s.r. tube was performed in the same manner as described previously[2]. The e.s.r. spectrum of the reaction mixture was recorded at room temperature by a JES-ME-3X spectrometer with 100 kHz field modulation.

Molecular weight ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distribution (*MWD*) of the resulting polymer were determined by gel permeation chromatography (g.p.c.) (ALC 244, Water Associates), where tetrahydrofuran was used as eluent.

From an ethyl acetate (AcOEt) solution of NPMAm–MMA block copolymer a thin film was prepared and supplied for transmission electron microscopic examination.

RESULTS AND DISCUSSION

Homopolymerization of NPMAm

The homopolymerizability of NPMAm was examined thermally and photochemically in benzene. The polymeri-

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Table 1 Homopolymerization of NPMAm with AIBN in benzene[a]

Temperature (°C)	Time (h)	Amount of AIBN added ($\times 10^3$) (g)	Yield (%)
40	3	8.8	16
40	6	8.8	44
40	10	8.8	74
40	6	88	87
50	6	8.8	91
50	6	88	95
60	6	9.1	96
70	6	8.8	97

[a] NPMAm, 0.4 g; benzene, 2 ml

Table 2 Photosensitized polymerization of NPMAm in benzene by using DBPO as sensitizer[a]

Amount of NPMAm (g)	Time (h)	Yield (%)
0.5	3	89
0.5	5	93
0.4	5	94

[a] A solution of NPMAm and DBPO (0.05 ml) in benzene (2 ml) was irradiated at room temperature by a high-pressure mercury lamp (100 W)

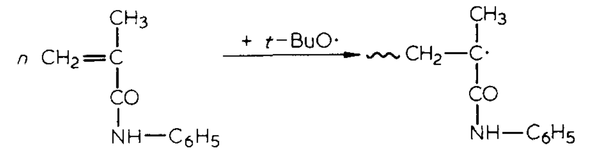
zation proceeded heterogeneously because poly(NPMAm) is insoluble in benzene.

Table 1 summarizes the results of the polymerization of NPMAm with AIBN. The polymer yield increased with increases in the AIBN concentration, polymerization time and temperature. Almost quantitative yield (95–97%) was observed in the polymerization at 50°–70°C for 6 h.

Table 2 shows the results obtained in the photosensitized polymerization of NPMAm by using DBPO as sensitizer. Poly(NPMAm) was formed with high yield of 89–94% by u.v. irradiation for 3–5 h at room temperature.

Generation of the living poly(NPMAm) radical and its reaction with MMA

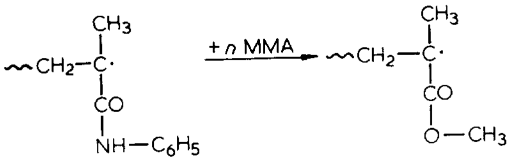
When NPMAm was photopolymerized at room temperature in benzene by using DBPO as sensitizer, the resulting propagating radical of NPMAm was found to be living in the heterogeneous polymerization system (equation (1)).



$$n\ CH_2{=}\overset{CH_3}{\underset{\underset{NH-C_6H_5}{CO}}{C}} \xrightarrow{+\ t\text{-}BuO\cdot} \sim CH_2-\overset{CH_3}{\underset{\underset{NH-C_6H_5}{CO}}{C}}\cdot$$

The e.s.r. spectrum of the polymerization mixture is shown in *Figure 1a*. The five-line spectrum observed is characteristic of the propagating polymer radicals stemming from methacrylate derivatives[2].

The spectrum in *Figure 1b* was obtained when the living poly(NPMAm) radical was allowed to react with MMA for 30 min at room temperature. This nine-line spectrum is assigned to the propagating polymer radical of MMA[2]. These findings reveal that poly(NPMAm) radical reacts easily with MMA to yield stable poly(MMA) radical under the present conditions (equation (2)).



$$\sim CH_2-\overset{CH_3}{\underset{\underset{NH-C_6H_5}{CO}}{C}}\cdot \xrightarrow{+\,n\ MMA} \sim CH_2-\overset{CH_3}{\underset{\underset{O-CH_3}{CO}}{C}}\cdot$$

Synthesis of block copolymer via the reaction of the living poly(NPMAm) radical with vinyl monomers

As described above, the photopolymerization of NPMAm at room temperature proceeds with high yield. The resulting polymerization mixture contains the stable poly(NPMAm) radical, which reacts readily with MMA to give poly(MMA) radical. This interesting observation led us to an attempt to prepare block copolymer by using the reaction of poly(NPMAm) radical with vinyl monomers.

Table 3 shows the results obtained when poly(NPMAm) radical was allowed to react with some vinyl monomers. The second monomers were MMA, methyl acrylate (MA), acrylonitrile (AN), styrene (St) and vinyl acetate (VAc). The reaction conditions are specified in the Table.

MMA and MA were found to be polymerized with a moderate yield. However, polymerizations of AN, St and VAc scarcely proceeded under the present conditions,

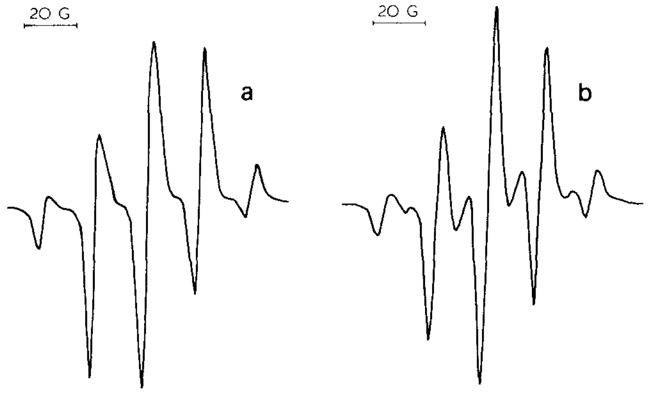


Figure 1 E.s.r. spectrum of the poly(NPMAm) radical/MMA system. (a) A benzene solution (0.3 ml) of NPMAm (0.55 mol l^{-1}) and DBPO (0.1 mol l^{-1}) in an e.s.r. tube was irradiated at room temperature for 3 h. (b) To the above polymerization mixture a benzene solution (0.5 ml) of MMA (5.6 mol l^{-1} was added and allowed to react at room temperature for 30 min

Table 3 Reaction of poly(NPMAm) radical with some vinyl monomers[a]

Second monomer (M_2)	Amount of M_2 (g)	Total yield (g)	Total yield (%)[b]	Recovered NPMAm (g)
MMA	1.88	1.07	37	0.02
MA	1.91	0.87	30	0.10
AN	1.61	0.31	~0	0.09
St	1.80	0.31	~0	0.09
VAc	1.86	0.25	~0	0.15

[a] A solution of NPMAm (0.4 g) and DBPO (0.05 ml) in benzene (2 ml) was irradiated at room temperature for 5 h, and then the second monomer was added and allowed to react at 40°C for 30 h

[b] Based on the second monomer used

Table 4 Reaction of poly(NPMAm) radical with MMA[a]

Run	Temperature (°C)	Time (h)	Total yield (g)	(%)[b]	Recovered NPMAm (g)
1	40	30	1.07	37	0.02
2	30	20	0.48	8	0.06
3	20	30	0.73	21	0.07
4	20	20	0.32	8	0.21
5	20	10	0.29	5	0.21
6	10	30	0.64	18	0.11
7	10	20	0.33	5	0.18

[a] The reaction was carried out in the same manner described in *Table 3*. NPMAm, 0.4 g; MMA, 1.88 g

[b] Based on MMA added

Table 5 Fractionation of the polymer mixture formed in the NPMAm/MMA and NPMAm/MA systems

Run[a]	Part A[b] (%)	Part B[c] (%)	Part C[d] (%)
1	32	34	34
2	5	41	54
3	6	56	38
4	14	28	58
5	3	31	66
6	14	51	35
7	3	37	60
8[e]	10	61	29

[a] Same as described in *Table 4*

[b] Part A: insoluble in a AcOEt/MeOH (1:7 (v/v)) mixture and soluble in benzene

[c] Part B: insoluble in the AcOEt/MeOH mixture and insoluble in benzene

[d] Part C: soluble in the AcOEt/MeOH mixture and insoluble in benzene

[e] Second monomer: MA (in *Table 3*)

judging from the yield and i.r. spectrum of the resulting polymer. VAc, a non-conjugative monomer, is considered to have only slight reactivity towards poly(NPMAm) radical[5]. AN seems to accelerate bimolecular termination of poly(NPMAm) radical since AN is a very good solvent for poly(NPMAm). The reason for the low polymerizability of St is obscure at present, although the radical polymerization of St is well known to proceed much more slowly than that of acrylate monomers[6].

The reaction of poly(NPMAm) radical with MMA was further investigated on varying the reaction conditions. The observed results are summarized in *Table 4*. Elongation of the reaction time led to increase in the conversion of MMA. The temperature effect on the MMA conversion was, however, not substantial in the range from 10° to 40°C.

The amount of NPMAm monomer recovered differed a fair amount for different runs. (*Tables 3* and *4*). This probably originates from the fact that the polymerization of NPMAm in this system was initiated photochemically and proceeded heterogeneously. However, the amount of NPMAm recovered had a tendency to decrease with increase of the MMA conversion. This suggests that a small amount of NPMAm is incorporated in the MMA block in the post-polymerization.

The polymer mixtures formed from the reaction of poly(NPMAm) radical with MMA and MA were fractionated into three parts by selective precipitation. Part A is insoluble in an AcOEt/MeOH (1:7 (v/v)) mixture and soluble in benzene. Part B is insoluble in the AcOEt/MeOH mixture and insoluble in benzene. Part C is soluble in the AcOEt/MeOH mixture and insoluble in benzene. The results of fractionation are summarized in *Table 5*.

Figure 2 shows i.r. spectra of the fractionated parts obtained in run 1. I.r. spectra of parts A and C are nearly identical with those of poly(MMA) and poly(NPMAm), respectively. As expected, part B shows absorption bands due to both poly(MMA) and poly(NPMAm). These findings indicate that the block copolymer formed in this system was satisfactorily isolated as part B. Block copolymer was found to constitute 28–56% of the total polymer obtained.

The fractionation of the polymer formed in the poly(NPMAm) radical/MA system was not as satisfactory as in the MMA system. As can be seen from *Figure 3*,

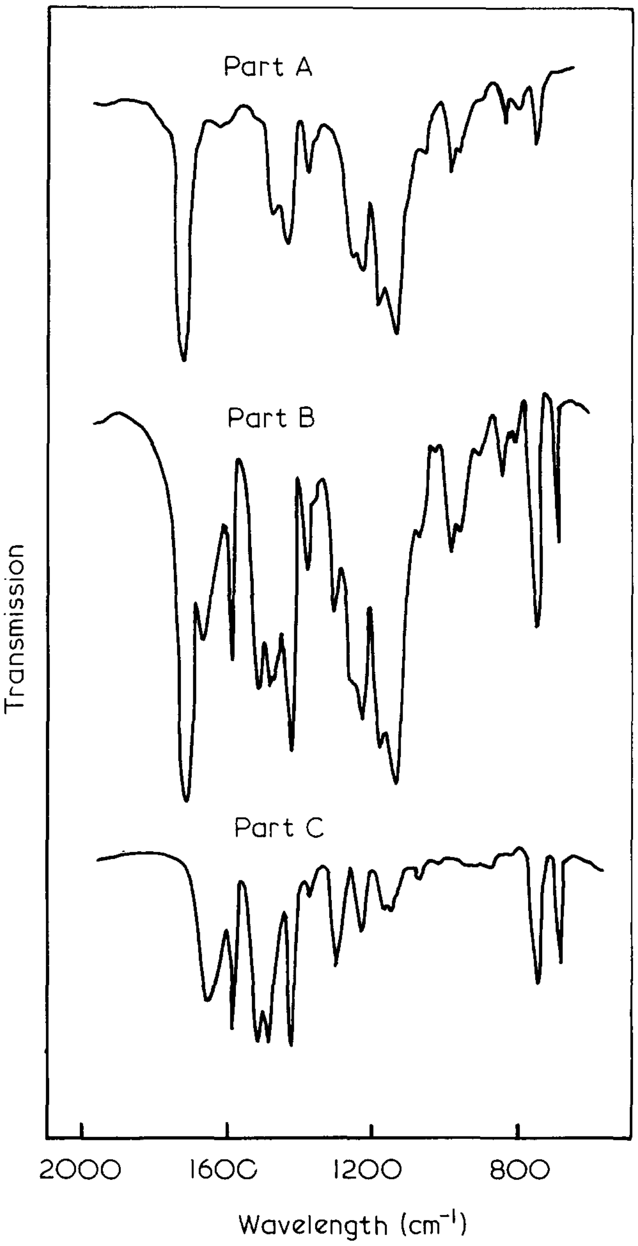


Figure 2 I.r. spectra of the fractionated polymers in the NPMAm/MMA system (run 1)

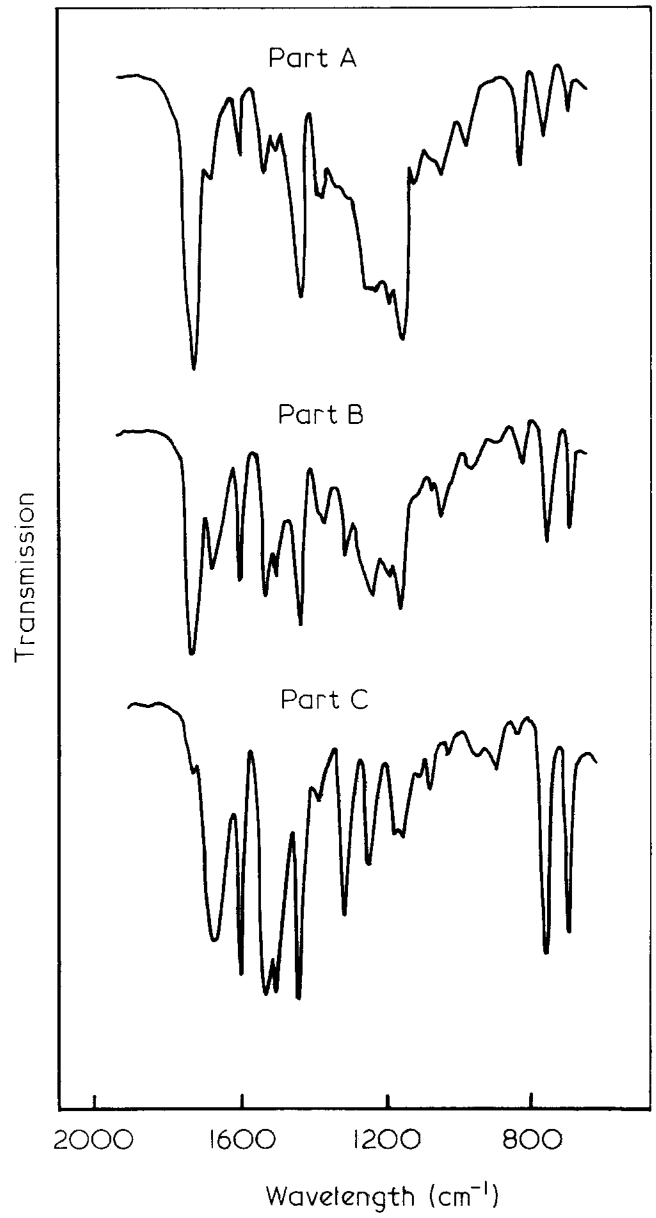


Figure 3 I.r. spectra of the fractionated polymers in the NPMAm/MA system (run 8)

Table 6 Molecular weight and polydispersity of parts B and C obtained in run 1

Sample	$\overline{M}_n$ (x10^{-4})	$\overline{M}_w$ (x10^{-4})	$\overline{M}_w/\overline{M}_n$
Part B	54.7	241.3	4.4
Part C	5.1	78.8	15.5
Poly(NPMAm)[a]	5.3	94.8	17.9

[a] Separately prepared under the same conditions as in the pre-polymerization in run 1

the i.r. spectrum of part A exhibits a small absorption peak due to amide group, while that of part C exhibits one due to ester carbonyl group. This observation reveals that parts A and C both contain a small amount of block copolymer. Hence, the amount of block copolymer in the NPMAm–MA system is more than 60% of the total polymer yield.

Figure 4 shows g.p.c. curves of parts B and C obtained in the NPMAm/MMA system (run 1). The g.p.c. curve of the homopolymer of NPMAm formed under the same conditions as in the pre-polymerization of NPMAm is also shown in this Figure for comparison. From these g.p.c.

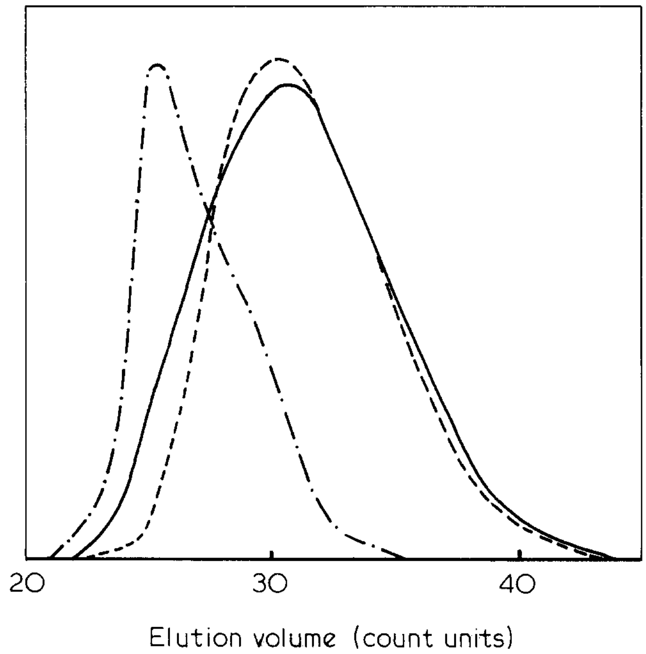


Figure 4 G.p.c. curves of parts B (–·–) and C (– – –) in run 1, and separately prepared poly(NPMAm) (——)

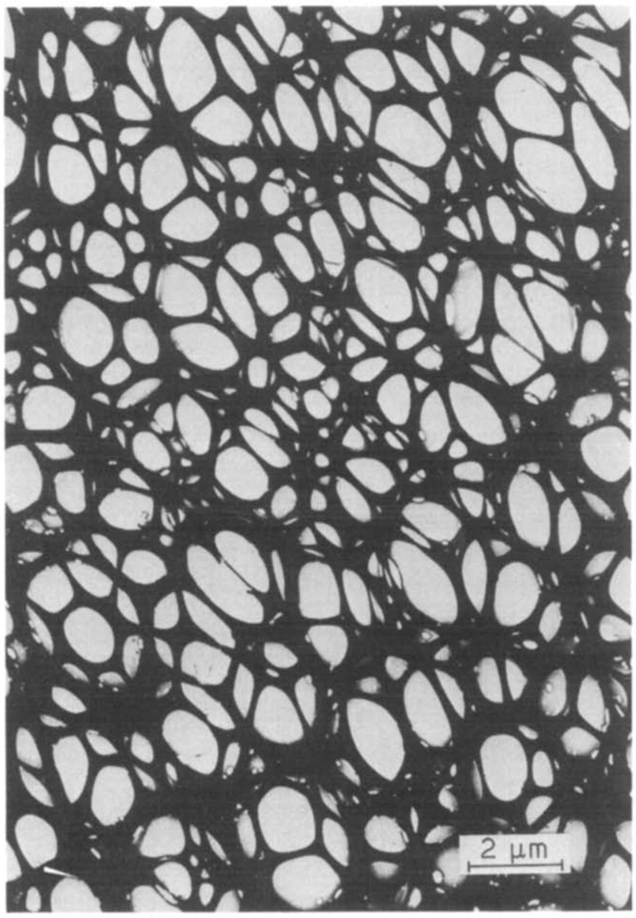


Figure 5 Transmission electron micrograph of NPMAm–MMA block copolymer (part B in run 1)

curves, $\bar{M}_n$, $\bar{M}_w$ and *MWD* were calculated and are summarized in *Table 6*. G.p.c. curves of part C and the separately prepared poly(NPMAm) are similar. So the broad *MWD* of these polymers stems from the fact that the heterogeneous photopolymerization was allowed to proceed up to high conversion. It is apparent from the g.p.c. results that block copolymer as part B has considerably higher molecular weight and narrower *MWD* compared with the parent poly(NPMAm).

Figure 5 shows a transmission electronic micrograph of a thin film which was prepared from an AcOEt solution of part B in run 1. A sea–island structure was clearly observed. The occurrence of such a microphase separation supports the assumption that this polymer is a block copolymer.

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