Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Sato, Tsuneyuki , Ogawa, Tetsuo and Otsu, Takayuki(1986) 'Grafting of Vinyl Monomers onto Poly(Acryloyl-L-valine) Microspheres Containing Peroxyester Groups', Journal of Macromolecular Science, Part A, 23: 8, 993 — 1005

To link to this Article: DOI: 10.1080/00222338608081106

URL: http://dx.doi.org/10.1080/00222338608081106

J. MACROMOL. SCI.–CHEM., A23(8), pp. 993-1005 (1986)

Grafting of Vinyl Monomers onto Poly(Acryloyl-L-valine) Microspheres Containing Peroxyester Groups

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ABSTRACT

Poly(acryloyl-L-valine) microspheres containing peroxyester groups were prepared by copolymerization of acryloyl-L-valine with di-t-butyl peroxyfumarate in acetophenone. Graft copolymerization of some vinyl monomers onto the microspheres was carried out by photolysis or thermolysis of the peroxyester groups in the microspheres. When benzyl methacrylate (BzMA) was used as the second monomer, BzMA conversion and grafting efficiency were found to increase with time. This might be ascribed to long lifetime of the polymer radicals in the microspheres. In fact, the very stable propagating radical of BzMA was observed by ESR in the photoinduced graft copolymerization system of the microspheres and BzMA at room temperature. The copolymerization process was investigated by ESR.

0022-233X/86/2308-0993$3.50/0

INTRODUCTION

N-Methylacrylamide and N-methylmethacrylamide have been polymerized by radical initiators in appropriate solvents to form polymer microspheres which contain the living propagating radicals of the amide monomers [1-3].

Recently, we found that N-acryloyl-L-valine (ALV) similarly forms polymer microspheres when it is polymerized in acetophenone. In a preceding paper [4], graft copolymerization of benzyl methacrylate (BzMA) onto poly(ALV) microspheres was attempted by using the photoreaction of carboxyl groups in poly(ALV) with lead tetraacetate. For this paper we prepared poly(ALV) microspheres containing t-butyl peroxyester groups by radical copolymerization of ALV with di-t-butyl peroxyfumarate (DBPF) in acetophenone. Further, graft copolymers were synthesized by photolysis or thermolysis of the peroxyester group in the presence of vinyl monomers. The photo-induced graft copolymerization was investigated by ESR spectroscopy.

EXPERIMENTAL

ALV was prepared by the reaction of acryloyl chloride with sodium salt of L-valine according to the method of Kulkarni [5] and recrystallized from ethyl acetate (AcOEt) (mp 123°C). DBPF was prepared by the reaction of fumaroyl chloride with sodium t-butyl hydroperoxide [6] and recrystallized from n-pentane (mp 34°C). Other monomers and solvents were used after standard purification.

Copolymerization of ALV (1 g) with a small amount (0.15 g) of DBPF by 2,2'-azobis-(2,4-dimethylvaleronitrile) (AVN), a low-temperature initiator, was performed in acetophenone at 40°C in a degassed sealed tube. The resulting poly(ALV) microspheres carrying t-butyl peroxyester groups were isolated by pouring the polymerization mixture into a large amount of toluene. The content of t-butyl peroxyester group in copoly(ALV-DBPF) was determined by iodometry according to the method of Silbert et al. [7].

Graft copolymerization of vinyl monomers onto copoly(ALV-DBPF) microspheres in benzonitrile was carried out thermally and photochemically in a degassed sealed tube. A high-pressure mercury lamp (100 W) was used as light source. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of ether. The isolated polymer mixture was divided into AcOEt-soluble and -insoluble parts by extracting with a large amount of AcOEt for a day at room temperature. The AcOEt-insoluble part was taken as graft copolymer.

ESR measurement of the graft copolymerization system was performed at room temperature by using a JES-ME-3X spectrometer with 100 kHz field modulation.

RESULTS AND DISCUSSION

Preparation of Copoly(ALV-DBPF) Microspheres

Poly(ALV) microspheres bearing t-butyl peroxyester groups were prepared by copolymerization of ALV with a small amount (9.1 mol%) of DBPF at 40°C in acetophenone by AVN. The copolymer was determined to contain 1.9 mol% of the DBPF monomer unit by iodometry. The resulting copoly(ALV-DBPF) microspheres were found to be well swollen and dispersed in some aromatic solvents, such as benzene and benzonitrile [4].

ESR Study of Photolysis of Copoly(ALV-DBPF) Microspheres in Benzene

Figure 1 shows ESR spectra observed when copoly(ALV-DBPF) microspheres were irradiated in benzene at room temperature. Thus, long-lived polymer radicals were found to be easily formed by photolysis of t-butyl peroxyester groups in the microspheres although the radical could not be identified. About 90% of the polymer radicals survived 70 min after stopping irradiation. Even after 18 h, 15% of them were still living.

ESR Study of the Reaction of BzMA with the Microsphere Polymer Radicals

Figure 2 shows ESR spectra of the reaction mixture of photolysis of copoly(ALV-DBPF) microspheres in BzMA. The nine-line spectrum is assignable to the propagating radical of BzMA. These polymer radicals were so stable that 75% of them survived 18 h after stopping irradiation. Twenty percent of the polymer radicals were still living after 42 h. Thus, the microsphere polymer radicals reacted readily with BzMA to produce the long-lived propagating radicals stemming from BzMA in the microspheres, as shown in Figure 3.

Photoinduced Graft Copolymerization of BzMA onto Copoly(ALV-DBPF) Microspheres

As described above, UV irradiation of copoly(ALV-DBPF) microspheres was found to produce stable polymer radicals in the microspheres. These polymer radicals reacted readily with BzMA to yield the living propagating radicals of BzMA. These findings led us to attempt graft copolymerization of BzMA onto the microspheres.

Table 1 shows the results observed in the photoinduced graft co-

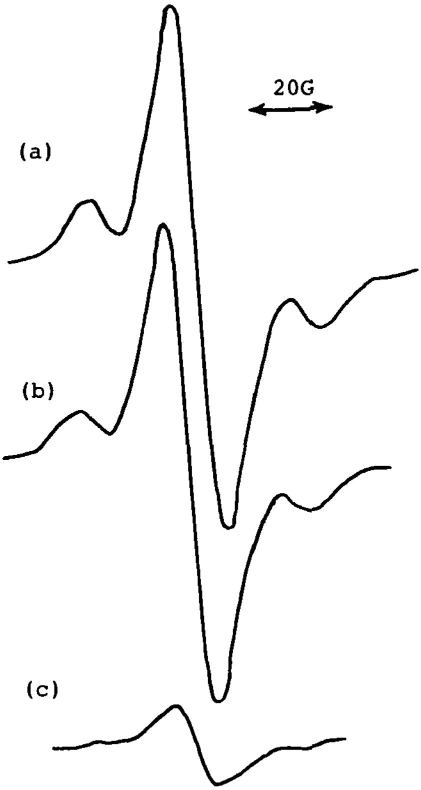

FIG. 1. ESR spectra observed in the photolysis of copoly(ALV-DBPF) microspheres in benzene at room temperature; (a) irradiated for 2 h, (b) 70 min after stopping irradiation, (c) 18 h after stopping irradiation.

polymerization in benzonitrile at 30°C. Conversion of BzMA and grafting efficiency [(weight of grafted poly(BzMA)/total weight of poly(BzMA)) × 100] increased with irradiation time. One reason for the increase in grafting efficiency is considered to be further propagation of the accumulated living poly(BzMA) radicals in the microspheres. Another one is the reaction between t-butoxy radicals formed in the microspheres and benzylic hydrogens of grafted poly(BzMA), the possibility of which is considered to increase with an increasing amount of grafted poly(BzMA).

An increasing quantity of BzMA resulted in a decrease in grafting efficiency. This might be ascribed to chain transfer reaction of the microsphere polymer radicals to BzMA monomer carrying labile benzylic hydrogens.

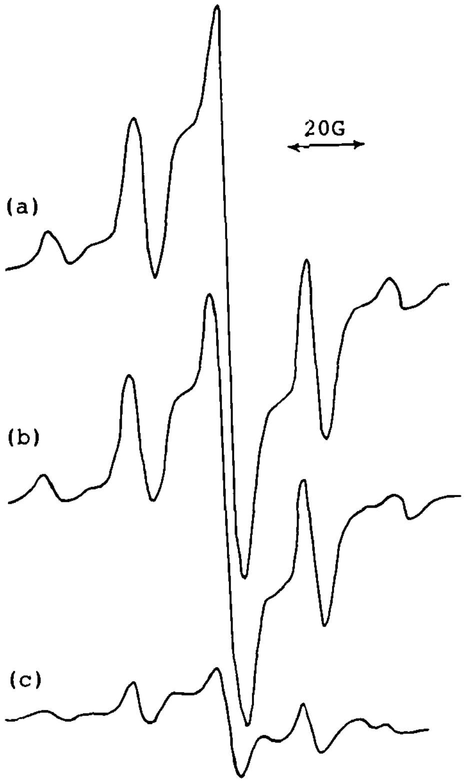

FIG. 2. ESR spectra observed in the photolysis of copoly(ALV-DBPF) microspheres in BzMA at room temperature: (a) irradiated for 3.5 h, (b) 18 h after stopping irradiation, (c) 42 h after stopping irradiation.

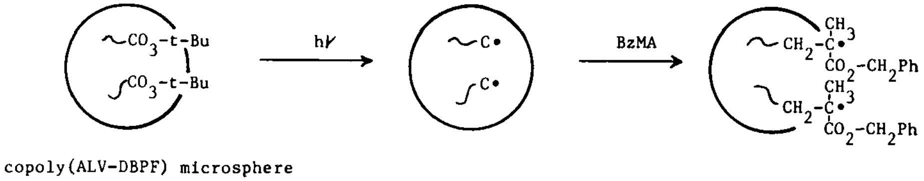

FIG. 3. Schematic picture for the formation of long-lived poly-(BzMA) radical in copoly(ALV-DBPF) microspheres.

TABLE 1. Photoinduced Graft Copolymerization of BzMA onto Copoly(ALV-DBPF) Microspheres at 30°C in Benzonitrile[a]

Run	BzMA, g	Time, h	Conversion of BzMA, %	Grafting efficiency, %	Weight increase of polymer,[b] %
1	2.08	1	15.5	17.7	65
2	2.08	3	40.7	23.9	260
3	2.08	5	57.5	27.8	408
4	1.04	3	42.2	25.0	141
5	3.12	3	37.8	20.1	275
6	4.16	3	25.2	4.8	70

[a] A mixture of copoly(ALV-DBPF) (0.08 g)/BzMA/benzonitrile was irradiated. [BzMA] + [benzonitrile] = 4 mL.

[b] {[Wt of graft copolymer - wt of copoly(ALV-DBPF)] /wt of copoly(ALV-DBPF)} × 100.

Thermal Graft Copolymerization of BzMA onto Copoly(ALV-DBPF) Microspheres

Peroxyester groups are known to decompose into free radicals at relatively high temperatures [8]. Therefore, graft copolymerization of BzMA onto copoly(ALV-DBPF) microspheres was carried out in the range 50-90°C in benzonitrile. The results are summarized in Table 2. As shown in Fig. 4, conversion of BzMA increased with time. Grafting efficiency also showed a tendency to increase with time. The increase in grafting efficiency might be ascribable to the long lifetime of the polymer radicals formed in the microspheres, which can propagate for a long time. Further, newly formed t-butoxy radicals can react with grafted poly(BzMA) before escaping from the microspheres into the bulk.

Increasing temperature resulted in increases both in BzMA conversion and grafting efficiency. Similar to photoinduced graft copolymerization, grafting efficiency decreased with increasing concentration of the monomer although BzMA conversion was almost unaltered. Further, as shown in Table 3, an increasing quantity of copoly(ALV-DBPF)

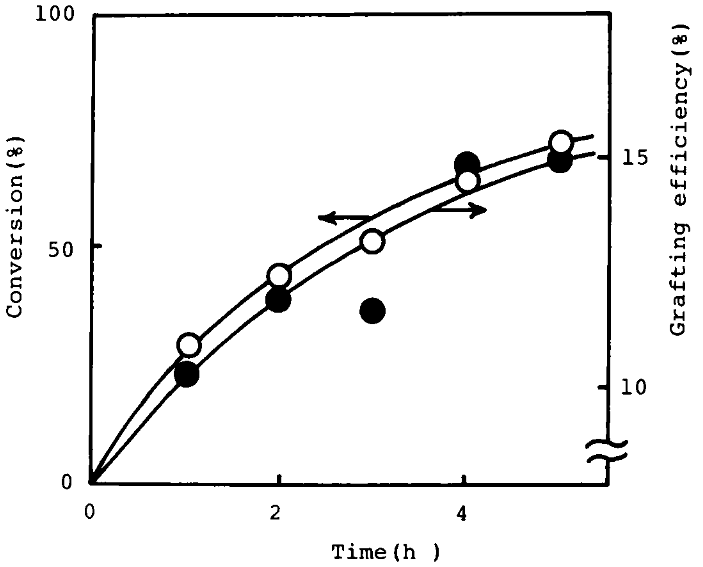

FIG. 4. Time-conversion (○) and time-grafting efficiency (●) curves in graft copolymerization of BzMA onto copoly(ALV-DBPF) microspheres at 80°C in benzonitrile. Reaction conditions as shown in Table 2.

TABLE 2. Thermal Graft Copolymerization of BzMA onto Copoly(ALV-DBPF) Microspheres in Benzonitrile[a]

Run	BzMA, g	Temperature, °C	Time, h	Conversion of BzMA, %	Grafting efficiency, %	Weight increase of polymer,[b] %
7	2.08	80	1	28.6	10.4	87
8	2.08	80	2	42.3	11.8	128
9	2.08	80	3	51.3	11.6	159
10	2.08	80	4	64.3	14.6	255
11	2.08	80	5	72.2	14.9	275
12	2.08	50	3	9.4	3.7	11
13	2.08	60	3	19.6	10.0	47
14	2.08	65	3	29.8	10.9	84
15	2.08	90	3	74.5	16.5	308
16	1.04	80	3	60.0	17.6	140
17	3.12	80	3	58.4	9.5	209
18	4.16	80	3	62.1	7.2	233

[a] A mixture of copoly(ALV-DBPF) (0.08 g)/BzMA/benzonitrile was heated. [BzMA] + [benzonitrile] = 4 mL.

[b] See Table 1, footnote b.

TABLE 3. Effect of Quantity of Copoly(ALV-DBPF) Microspheres on Thermal Graft Copolymerization of BzMA for 3 h at 80°C in Benzonitrile[a]

Run	Copoly(ALV-DBPF), g	Conversion of BzMA, %	Grafting efficiency, %	Weight increase of polymer,[b] %
19	0.04	40.3	9.1	208
9	0.08	51.3	11.6	159
20	0.16	69.8	20.8	192
21	0.32	87.0	28.8	166

[a] A mixture of copoly(ALV-DBPF)/BzMA (2 mL)/benzonitrile (2 mL) was heated.

[b] See Table 1, footnote b.

microspheres was found to increase both BzMA conversion and grafting efficiency.

Graft Copolymerization of Some Vinyl Monomers onto Copoly(ALV-DBPF) Microspheres

Graft copolymerization in benzonitrile of some other monomers was also attempted. The monomers used were methyl acrylate (MA), vinyl acetate (VAc), methyl methacrylate (MMA), and styrene (St).

Table 4 shows the results of photoinduced graft copolymerization. Although the acrylate monomers showed relatively high conversions, the polymerizations of St and VAc scarcely proceeded under the present conditions.

Table 5 summarizes the results of thermal graft copolymerization at 80°C. Conversions of St and VAc were higher than those in the photoinduced graft copolymerization. MA showed higher conversion and lower grafting efficiency than BzMA. On the other hand, MMA was found to give a similar conversion and a higher grafting efficiency.

Characterization of Graft Copolymer

Figure 5 shows IR spectra of the AcOEt-soluble and -insoluble parts obtained in the thermal graft copolymerization of BzMA onto the microspheres (Run 15), together with that of the parent copoly(ALV-DBPF). The spectrum of the AcOEt-soluble part was almost identical with that of poly(BzMA). As anticipated, the insoluble part showed absorption bands due to both poly(BzMA) and poly(ALV).

Some graft copolymers are known to form a microphase-separated structure owing to the different physical properties of different polymer chains [9]. The graft copolymer obtained in the present system was also found to exhibit microphase separation. Figure 6 shows an electron micrograph of a thin film prepared from a dilute THF solution (0.14%) of the graft copolymer (Run 11).

TABLE 4. Photoinduced Graft Copolymerization of Some Vinyl Monomers onto Copoly(ALV-DBPF) Microspheres at 30°C in Benzonitrile[a]

	Monomer				
Run	Type	Amount, g	Conversion, %	Grafting efficiency, %	Weight increase of polymer,[b] %
2	BzMA	2.08	40.7	23.9	260
22	MA	1.91	93.5	15.1	373
23	VAc	1.86	0	-	-
24	MMA	1.88	25.8	25.4	164
25	St	1.80	1.0	-	-

[a] A mixture of copoly(ALV-DBPF) (0.08 g)/monomer/benzonitrile (2 mL) was irradiated for 3 h.
[b] See Table 1, footnote b.

TABLE 5. Thermal Graft Copolymerization of Some Vinyl Monomers onto Copoly(ALV-DBPF) Microspheres for 3 h at 80°C in Benzonitrile[a]

	Monomer				
Run	Type	Amount, g	Conversion, %	Grafting efficiency, %	Weight increase of polymer,[b] %
9	BzMA	2.08	51.3	11.6	159
26	MA	1.91	91.7	6.2	144
27	VAc	1.86	11.1	27.9	74
28	MMA	1.88	49.5	19.3	228
29	St	1.80	6.5	9.5	13

[a] A mixture of copoly(ALV-DBPF) (0.08 g)/monomer/benzonitrile (4 mL) was heated.
[b] See Table 1, footnote b.

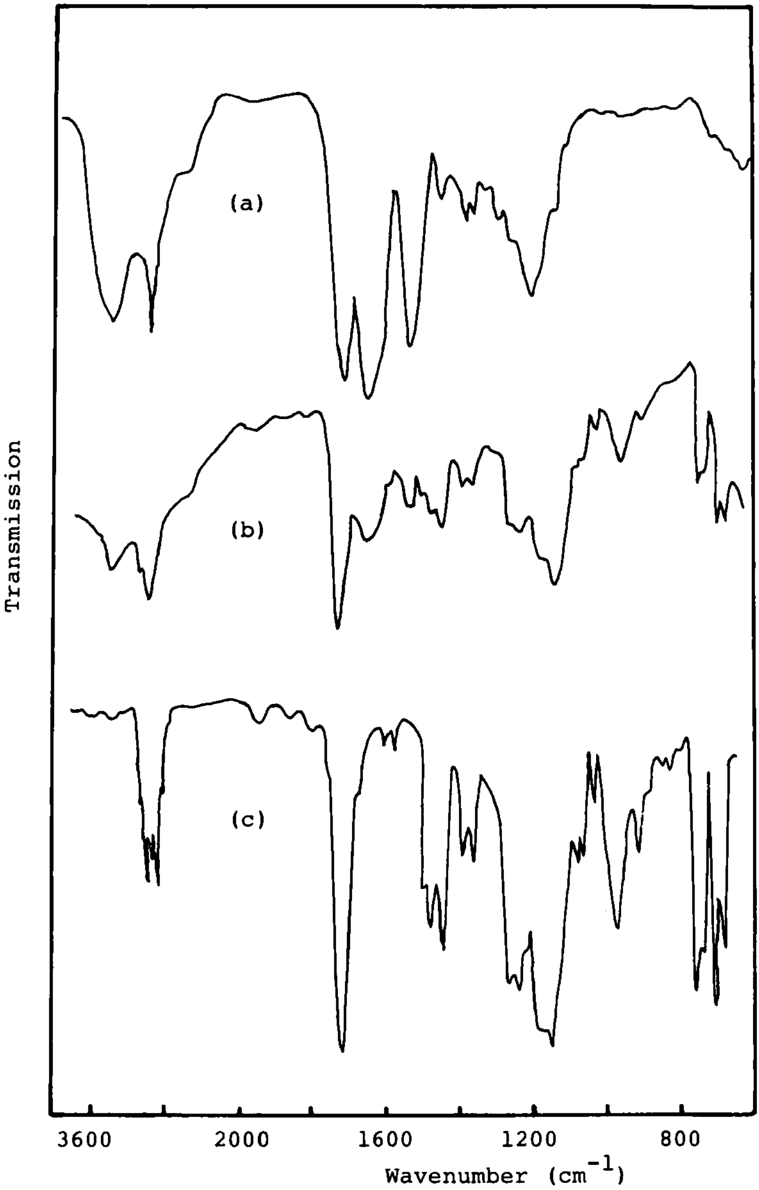

FIG. 5. IR spectra of copoly(ALV-DBPF) (a), the insoluble (b), and soluble (c) parts (Run 15).

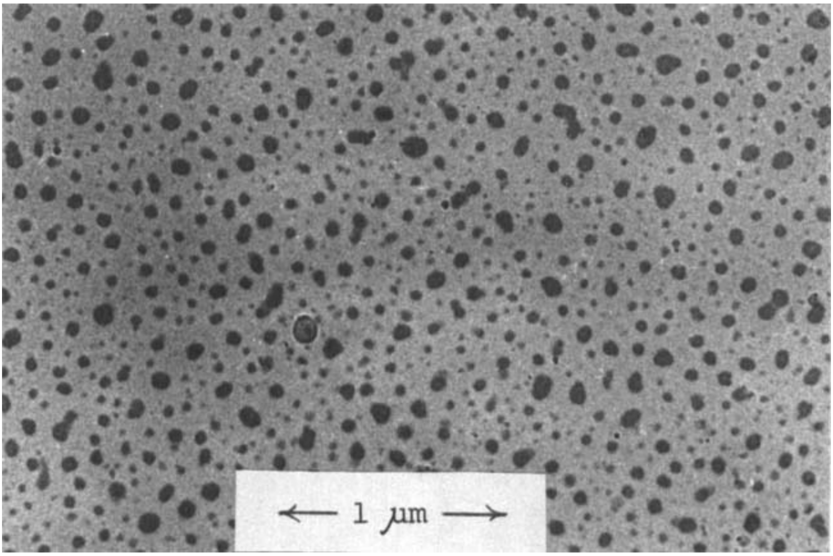

FIG. 6. Transmission electron micrograph of a thin film of graft copolymer (Run 11).

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Received July 16, 1985