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Graft Copolymerization of Benzyl Methacrylate onto Poly(Acryloyl-L-valine) Microspheres by Using the Photoreaction of Side Carboxyl Groups with Lead Tetraacetate

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ABSTRACT

N-Acryloyl-L-valine (ALV) was found to yield polymer microspheres when it was polymerized with a radical initiator in acetophenone. The resulting microspheres showed thermochromism in aromatic solvents such as benzonitrile, methyl benzoate, and acetophenone. Graft copolymerization of benzyl methacrylate (BzMA) onto poly(ALV) microspheres was carried out in benzonitrile by using the photoreaction of carboxyl groups in poly(ALV) with $Pb(OAc)_4$. The grafting efficiency was not very high (15-28%).

Methyl methacrylate as the second monomer gave a higher grafting efficiency (56%) although the polymer yield was considerably lower. The resulting graft copolymer was characterized by IR spectroscopy and thermogravimetry. The grafted poly(ALV) microspheres were well dispersed in benzene. A benzene solution of grafted poly(ALV) microspheres and homopoly(BzMA) gave a film with finely dispersed poly(ALV) microspheres.

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INTRODUCTION

In previous papers [1-3] we reported that amide monomers such as N-methylacrylamide (NMAAm) and N-methylmethacrylamide (NMMAm) were polymerized with radical initiators to form polymer microspheres that were dispersed in the polymerization systems. Further, the microspheres were found to contain living propagating polymer radicals of the amide monomers.

We recently found that N-acryloyl-L-valine (ALV), a monosubstituted amide monomer, also yielded microspheres when ALV was polymerized in acetophenone.

Since carboxylic acids are known to produce free radicals by reaction with lead tetraacetate ($Pb(OAc)_4$) under UV irradiation [4, 5], we have attempted graft copolymerization of benzyl methacrylate (BzMA) onto poly(ALV) microspheres by using the photoreaction of carboxyl groups in poly(ALV) with $Pb(OAc)_4$. This paper describes the formation of poly(ALV) microspheres and the results of the graft copolymerization.

EXPERIMENTAL

ALV was prepared by the reaction of acryloyl chloride with L-valine in the presence of sodium hydroxide according to the method of Kulkarni et al. [6] and recrystallized from ethyl acetate (AcOEt) (mp 123°C). Commercial $PB(OAc)_4$ (Wako Pure Chemical Industries) was used without further purification. Other monomers, di-t-butyl peroxide (DBPO) (photoinitiator) and solvents were purified by distillation.

Poly(ALV) microspheres were prepared by photopolymerization of ALV with DBPO for 5 h at 30°C in acetophenone in a degassed sealed tube by using a high-pressure mercury lamp (100 W). The resulting poly(ALV) microspheres were isolated by pouring the polymerization mixture into a large excess of toluene.

Graft copolymerization of vinyl monomers onto poly(ALV) microspheres was carried out in the following manner. Poly(ALV) microspheres were dispersed in benzonitrile in a glass tube, and then a second monomer and $Pb(OAc)_4$ were added. The system was deaerated by the freezing and thawing method and sealed under vacuum. After UV irradiation by a high-pressure mercury lamp (100 W) for a given time at 30°C, the polymerization mixture was separated into AcOEt-soluble and insoluble parts by extracting with a large amount of AcOEt for 1 day at room temperature. The AcOEt-insoluble part was taken as graft copolymer.

Dynamic thermogravimetric (TG) behavior of the polymers was studied by using a thermogravimeter (Shimadzu TG-20) at a heating rate of 10°C/min in a nitrogen flow (25 mL/min). All runs were terminated at 550°C.

RESULTS AND DISCUSSION

Preparation of Poly(ALV) Microspheres

When ALV was photopolymerized with DBPO as photoinitiator in acetophenone, the resulting polymer was dispersed as microspheres in the polymerization system. This system showed a beautiful violet color owing to selective light scattering by the polymer microspheres. Figure 1 shows a scanning electron micrograph (SEM) of a sample prepared by vacuum evaporation of a benzonitrile solution containing dispersed poly(ALV) microspheres.

Similarly to the systems of aromatic solvents and poly(NMAAm) or poly(NMMAm) microspheres [7], poly(ALV) particles exhibited a thermochromism, as shown in Table 1, when they were dispersed

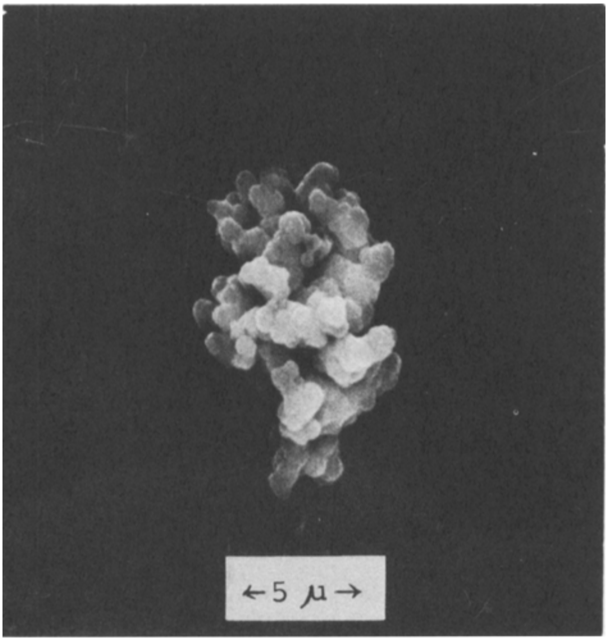

FIG. 1. SEM of poly(ALV) microspheres.

TABLE 1. Thermochromism of the System Poly(ALV) Microspheres/Methyl Benzoate

Temperature, °C	Color
10	Blue
20	Blue
30	Blue
40	Violet
50	Yellowish violet

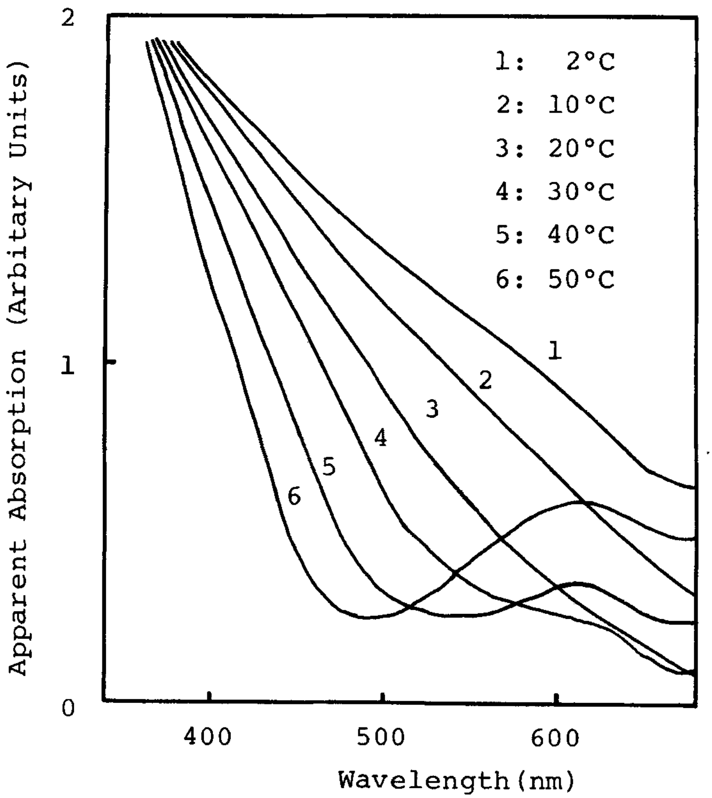

FIG. 2. Temperature effect on apparent absorption spectrum of the system poly(ALV) microspheres/methyl benzoate.

in methyl benzoate. This phenomenon is based on a Christiansen filter consisting of poly(ALV) microspheres and methyl benzoate [7]. Figure 2 shows the temperature effect on the apparent absorption spectrum of a solution of poly(ALV) microspheres dispersed in methyl benzoate.

Graft Copolymerization of BzMA onto Poly(ALV) Microspheres

The reaction of some carboxylic acids (R–COOH) and $Pb(OAc)_4$ under UV irradiation has been reported to yield free radical (R•) according to the following reactions [4, 5, 8]:

$$Pb^{IV}(OAc)_4 + R\text{–}COOH \rightleftharpoons \underset{(I)}{R\text{–}COOPb^{IV}(OAc)_3} + CH_3COOH, \quad (1)$$

$$I \xrightarrow{h\nu} R\cdot + CO_2 + Pb^{III}(OAc)_3. \quad (2)$$

The formation of radical R• was confirmed by a spin-trapping study [5].

We have attempted graft copolymerization by using the photoreaction of $Pb(OAc)_4$ with carboxyl groups in poly(ALV) microspheres. BzMA was mainly used as the second monomer because poly(ALV) microspheres were well swollen and dispersed in BzMA, an aromatic solvent. A mixture of poly(ALV) microspheres, BzMA, benzonitrile, and $Pb(OAc)_4$ was irradiated at 30°C.

Table 2 summarizes the results of the graft copolymerization of BzMA onto poly(ALV) microspheres. BzMA conversion and the weight increase of polymer ({[weight of the resulting graft copolymer - weight of poly(ALV)]/weight of poly(ALV)} × 100) were found to increase with irradiation time (Runs 1-4). Grafting efficiency ([weight of grafted poly(BzMA)/total weight of poly(BzMA)] × 100) was somewhat low (18-25%) and did not seem to depend upon the irradiation time.

Total conversion of BzMA, weight increase of the polymer, and grafting efficiency increased with increasing quantities of $Pb(OAc)_4$ (Runs 2, 5-7).

Contrary to the results observed for variation of the quantity of $Pb(OAc)_4$, BzMA conversion and grafting efficiency were found to be almost constant with increasing quantities of poly(ALV) (Runs 2, 6, 9). As a consequence, weight increase of the polymer fell. These findings indicate that the concentration of available carboxyl groups in poly-

TABLE 2. Photoinduced Graft Copolymerization of BzMA onto Poly(ALV) Microspheres at 30°C in Benzonitrile[a]

Run	Poly(ALV), g	$Pb(Ac)_4$, g	BzMA, g	Time, h	Conversion of BzMA, %	Grafting efficiency, %	Weight increase of polymer, %
1	0.08	0.02	2.08	3	34	15	134
2	0.08	0.02	2.08	5	45	24	283
3	0.08	0.02	2.08	7.5	54	20	285
4	0.08	0.02	2.08	10	72	25	432
5	0.08	0	2.08	5	22	12	65
6	0.08	0.01	2.08	5	43	19	207
7	0.08	0.04	2.08	5	58	28	420
8	0.14	0.02	2.08	5	44	21	135
9	0.20	0.02	2.08	5	40	23	97
10	0.08	0.02	1.05	5	53	25	169
11	0.08	0.02	4.16	5	50	15	381

[a] A mixture of poly(ALV)/BzMA/benzonitrile/$Pb(Ac)_4$ was irradiated. [BzMA] + [benzonitrile] = 4 mL.

(ALV) microspheres is much higher than that of $Pb(OAc)_4$ in spite of the heterogeneous system under the present conditions (see Eq. 1).

The effect of the quantity of BzMA on graft copolymerization was also examined (Runs 2, 10, 11). Similar BzMA conversions were observed for three different quantities of BzMA. Weight increase of the polymer rose with increasing quantities of BzMA. However, the grafting efficiency showed a tendency to decrease with increasing BzMA. This tendency may be attributed to the labile hydrogens of the α-methyl group in BzMA monomer for chain transfer reaction

Graft Copolymerization of Some Other Vinyl Monomers onto Poly(ALV) Microspheres

Table 3 shows the results obtained when methyl methacrylate (MMA), styrene (St), vinyl acetate (VAc), and N-(1-phenylethyl)acrylamide (NPEA) were used as the second monomer.

Compared with BzMA, MMA was found to give a higher grafting efficiency although polymer yield was considerably lower. Polymerizations of St and VAc did not proceed under the present conditions. On the other hand, NPEA was polymerized in high yield (89%), but grafting efficiency was very low.

Characterization of the Resulting Graft Copolymer

Figure 3 shows IR spectra of the AcOEt-soluble and insoluble parts of the product of the graft copolymerization of BzMA on poly(ALV)

TABLE 3. Photoinduced Graft Copolymerization of Some Vinyl Monomers onto Poly(ALV) Microspheres at 30°C[a]

2nd monomer		Conversion of 2nd monomer, %	Grafting efficiency, %	Weight increase of polymer, %
	g			
MMA	1.88	28	56	356
VAc	1.86	-	-	-
St	1.80	-	-	-
NPEA[b]	0.99	89	3	27

[a] Mixtures of poly(ALV) (0.08 g)/$Pb(Ac)_4$ (0.02 g)/2nd monomer/ benzonitrile (2 mL) were irradiated for 5 h.

[b] Benzonitrile, 3 mL.

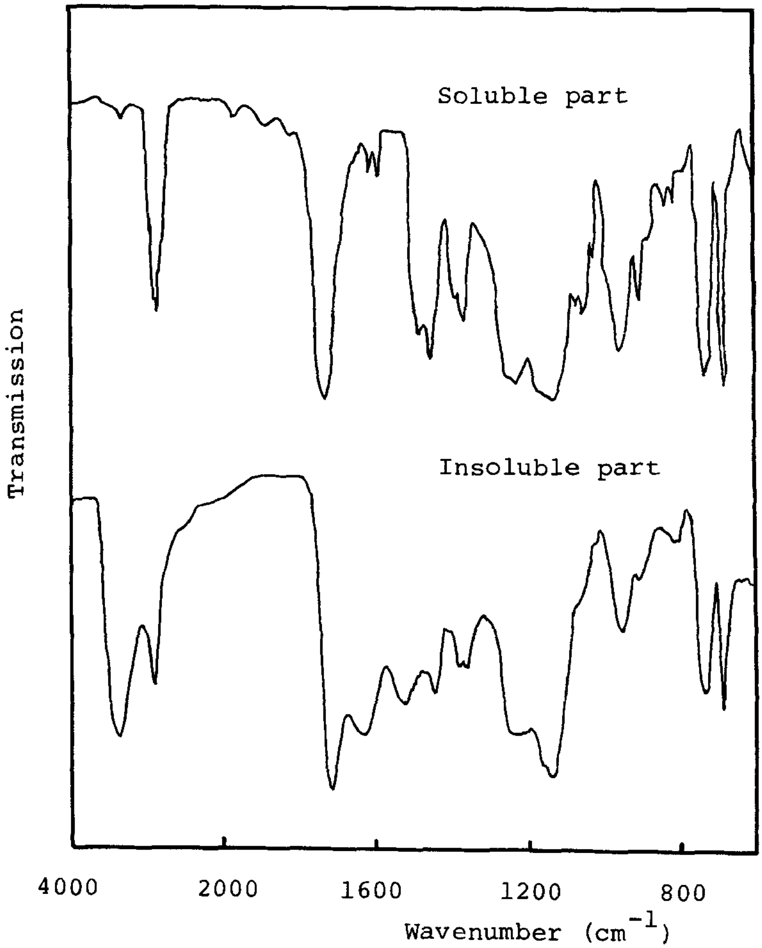

FIG. 3. IR spectra of the AcOEt-soluble and insoluble parts (Run 1).

microspheres (Run 1). As expected, the insoluble part showed absorption bands due to poly(ALV) and poly(BzMA), indicating that this part is a graft copolymer. On the other hand, the IR spectrum of the soluble part is closely similar to that of poly(BzMA).

Figure 4 shows TG and differential thermogravimetric (DTG) curves of the AcOEt-soluble and insoluble parts formed in Run 9, together with those of separately prepared poly(BzMA) for comparison. The insoluble part exhibited two main peaks around 300 and 380°C. Another graft copolymer of higher BzMA content was found

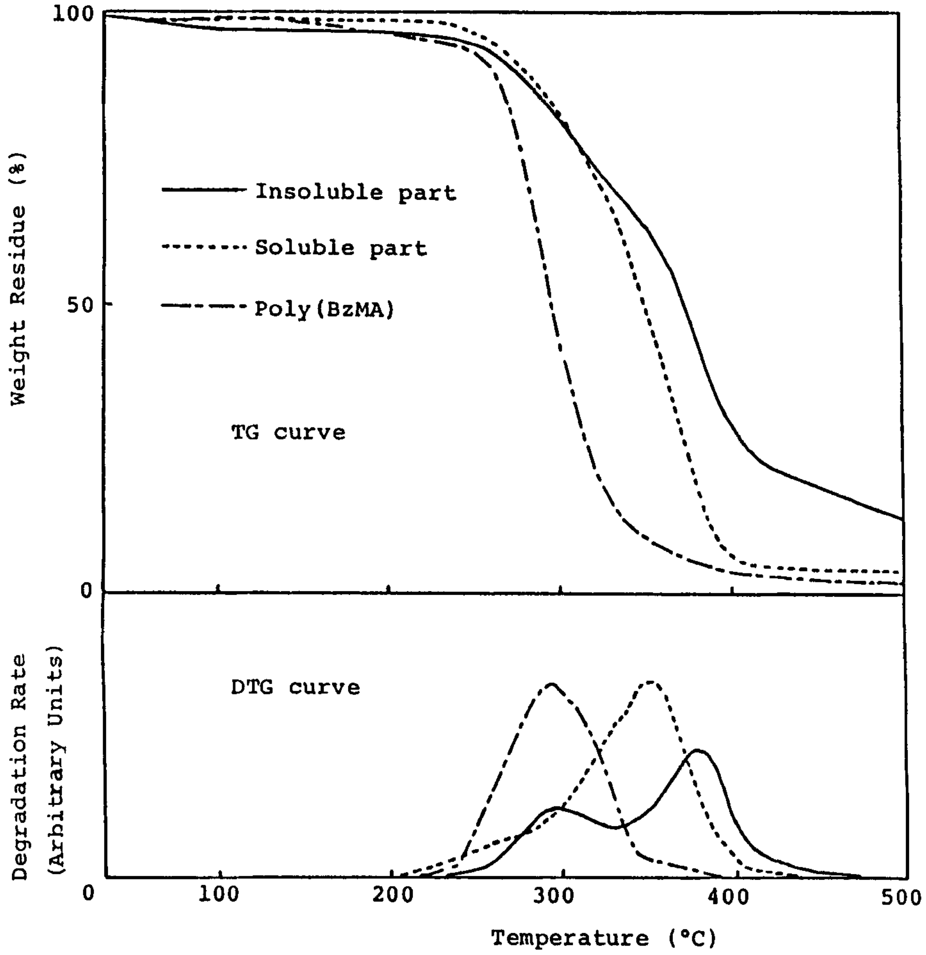

FIG. 4. TG and DTG curves of the AcOEt-soluble and insoluble parts (Run 9) and poly(BzMA).

to give a larger peak at 380°C, and hence the peak at 300°C seems to correspond to the poly(ALV) sequence. Homopoly(ALV) also showed a main peak around 300°C [9].

As shown in Fig. 4, the peak due to poly(BzMA) sequences was shifted to higher temperature in the following order; homopoly(BzMA < soluble part < insoluble part. It is suggested that poly(ALV) sequences retard the thermal degradation of poly(BzMA) sequences. The soluble part might contain short chains of poly(ALV) although they could not be detected in the IR spectrum. In the insoluble part, possible

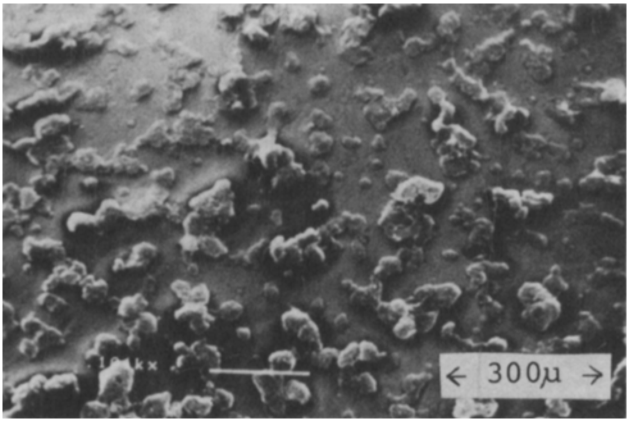

FIG. 5. SEM of a film prepared from poly(BzMA) and grafted poly(ALV) microspheres (Run 2).

crosslinking might also make some contribution to thermal stability of poly(BzMA) sequences.

Graft copolymerization of BzMA onto these poly(ALV)s is considered to give a sort of microspherical polymer bearing poly(BzMA) branches. In fact, the graft copolymer showed a better dispersion in benzene compared with the parent poly(ALV) microspheres. Therefore, a benzene solution containing poly(BzMA) and such graft copolymer is expected to yield a film with finely dispersed microspherical graft polymer. Figure 5 shows the SEM of a thin film which was prepared from a dilute benzene solution (~0.5%) of a 1:1 blend of BzMA-ALV (2:1) graft copolymer (Run 2) and poly(BzMA). Graft copolymer was observed as dispersed particles in Fig. 5. Such a film containing poly(ALV) microspheres as functional elements may find some uses in selective separation.

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