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Reactions

Long-Lived Polymer Radicals

7. Synthesis of Block Copolymers by the Reaction of Living Poly(N-Acryloyl-L-Valine) Radical with Vinyl Monomers

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Summary

When N-acryloyl-L-valine(ALV) was photo-polymerized in ethyl acetate, the resulting polymerization mixture was found to contain the living propagating radical of ALV. Synthesis of block copolymers was attempted by using the reaction of living poly(ALV) radical with some vinyl monomers. The resulting block copolymers were characterized by IR spectroscopy, dynamic thermogravimetry and pyrolysis gas chromatography.

Introduction

When some acrylamide derivatives are polymerized by radical initiators in adequate solvents, the resulting polymerization systems contain very stable propagating polymer radicals of the amide monomers(1,2). The living polymer radicals readily react with other vinyl monomers at room temperature to yield stable propagating polymer radicals of the second monomers(3,4). Further, synthesis of block copolymers was attempted by these reactions(5,6).

Recently, we have found that N-acryloyl-L-valine(ALV), an optically active amide monomer, is also polymerized in ethyl acetate(AcOEt) by radical initiators to give its living propagating radicals.

This paper concerns with the synthesis of block copolymers by using the reaction of living poly(ALV) radical with vinyl monomers.

Experimental

ALV was prepared by the reaction of L-valine with acryloyl chloride according to the method of Kulkarni et al(7), which was recrystallized from AcOEt(mp. 123°C, $[\alpha]_D$=-15.4°(C=4, in methanol at room temperature)). Other monomers, solvents and initiators were used after usual purifications. Polymerization and block copolymerization of ALV were carried out in a degassed sealed tube as described previously(6). The resulting polymer was isolated by pouring the polymerization mixture into a large excess of ether or AcOEt.

Dynamic themogravimetric(TG) curves and pyrolysis gas chromatograms of the resulting polymers were obtained by the same methods previously used(5). ESR measurement was carried out as described previously(3).

Results and Discussion

Homopolymerization of ALV

Polymerization of ALV was performed in AcOEt by using azobis-isobutyronitrile(AIBN) or photo-initiators(di-tert-butyl peroxide(DBPO) and 1,1′-azobis-cyclohexane-1-carbonitrile(ACN)). The polymerization proceeded heterogeneously because poly(ALV) was insoluble in AcOEt. The results obtained are presented in Table 1. Thus, ALV was found to be polymerized almost completely by the radical initiators under these conditions.

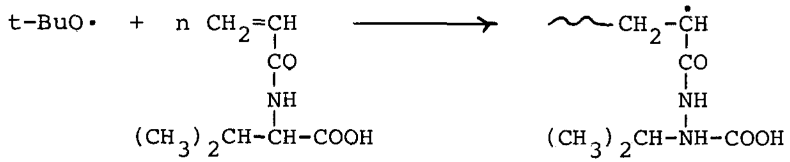
Table 1. Polymerization of ALV in AcOEt

Initiators (mol/l)	[ALV] (mol/l)	Temp. (°C)	Time (hr)	Yields (%)
AIBN (0.021)	0.65	60	5	~ 100
ACN + hν[a)] (0.049)	0.96	room temp.	1	~ 100
DBPO + hν[a)] (0.22)	0.96	room temp.	1	~ 100

a) A high pressure mercury lamp(100W) was used as light source.

Formation of Living Poly(ALV) Radical

Fig. 1 shows an ESR spectrum observed when ALV was photopolymerized in AcOEt by using DBPO as photo-sensitizer. The three-line spectrum was assigned to the propagating radical of ALV(I), which was formed according to the following reaction.



$$\text{t-BuO}\cdot + n\,\text{CH}_2\text{=CH(CO-NH-CH(COOH)CH(CH}_3)_2) \longrightarrow \sim\!\sim\text{CH}_2\text{-}\dot{\text{C}}\text{H(CO-NH-NH(COOH)CH(CH}_3)_2)$$

(ALV) (I)

Thus, living polymer radical(I) was easily produced in this heterogeneous polymerization system.

Reaction of Living Poly(ALV) Radical with Vinyl Monomers

The polymerization of ALV was found to proceed almost quantitatively in AcOEt. The resulting polymerization mixture contained living propagating radicals of ALV. Therefore, we have attempted to prepare block copolymers by using this system.

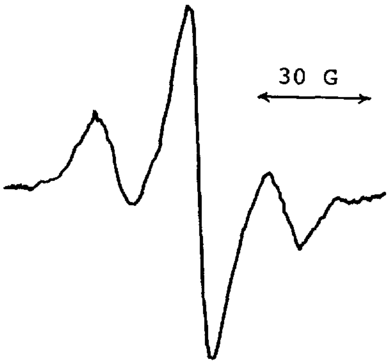


Fig. 1
ESR spectrum of the system ALV(0.06 g)/DBPO(0.05 ml)/AcOEt(0.7 ml)/$h\nu$

Table 2. Block copolymerization of ALV with vinyl monomers[a]

2nd monomers	(g)	Total yields (g)	(%)[b]	Sol. in AcOEt(%)	Sol. in MeOH(%)	Insol. (%)
MA-1	0.96	0.99	(82)	22.2	14.8	63.0
MA-2[c]	0.96	1.05	(89)	31.6	12.8	55.6
BA	0.91	0.33	(15)	44.2[d]	44.6	11.1
BzA	1.06	0.38	(17)	26.6	36.9	36.5
St	0.90	0.20	(0)	-	-	-
MMA	0.94	0.20	(0)	-	-	-
AN	0.81	0.20	(0)	-	-	-
MA/St[e]	0.93	0.30	(11)	17.1	43.4	39.4

[a] A mixture of ALV(0.2 g)/DBPO(0.05 ml)/AcOEt(1 ml) was irradiated for 1 hr at room temperature, and then a 2nd monomer(1 ml) was added and allowed to react for 48 hr at 40°C.

[b] Based on the 2nd monomer.

[c] ACN(1.46×10^{-2} mol/l) was used as photosensitizer.

[d] Soluble in benzene.

[e] A mixture of MA(0.5 ml) and St(0.5 ml).

A solution of ALV(0.2 g) and DBPO(0.05 ml) in AcOEt(1 ml) was irradiated by a high pressure mercury lamp(100 W) to yield living poly(ALV) radicals. Then, to this polymerization mixture a second monomer(1 ml) was added and allowed to react for 48 hr at 40°C. The second monomers used were methyl acrylate (MA), n-butyl acrylate(BA), benzyl acrylate(BzA), methyl methacrylate(MMA), acrylonitrile(AN) and styrene(St).

Table 2 shows the results. MA was polymerized in good yields(82, 89%) both in the systems of DBPO and ACN. Other acrylate monomers gave lower polymer yields(15-17%). On the other hand, the polymerizations of MMA, St and AN proceeded scarcely. A mixture of MA and St as the second monomer was found to be polymerized in a 11% yield.

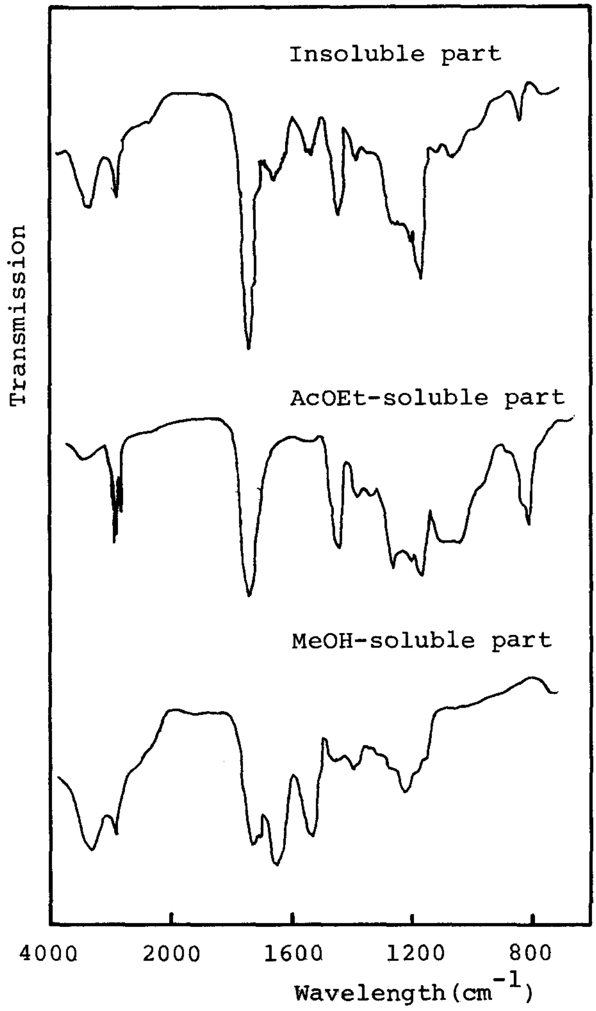


Fig. 2
IR spectra of the fractionated polymers in the ALV/MA system (MA-2)

The resulting polymer mixtures were fractionated into three parts by Soxhlet's extraction for 20 hr. AcOEt was first used as extracting solvent for homopolymers of the second monomers(benzene for poly(BA)). Second, poly(ALV) was extracted by methanol(MeOH). The insoluble residue was taken as block copolymer. The results of fractionation are also listed in Table 2. Block copolymer of the MA system consisted of 57-63% of the total polymer. The systems of BA and BzA gave lower block copolymer yields(11 and 37%, respectively).

Characterization of the Block Copolymers

The block copolymers formed were characterized by IR spectroscopy, TG and pyrolysis gas chromatography.

Fig. 2 shows IR spectra of the fractionated parts obtained in the MA system(MA-2 in Table 2). The spectra of AcOEt-soluble and MeOH-soluble parts were almost identical with those of poly(MA) and poly(ALV), respectively. As expected, the insoluble part as block copolymer showed absorption bands due to both poly(MA) and poly(ALV).

Fig. 3 shows TG and differential thermogravimetric(DTG) curves of each part. From these charts the insoluble part was also confirmed to consist of both poly(MA) and poly(ALV) sequences.

Fig. 4 shows a pyrogram of the insoluble part(MA-1 in Table 2), together with those of poly(MA) and poly(ALV). The pyrogram of the insoluble part appears to be an overlap of those of poly(MA) and poly(ALV). Another new peak was also observed for the insoluble part(A in Fig. 4) which might stem from the

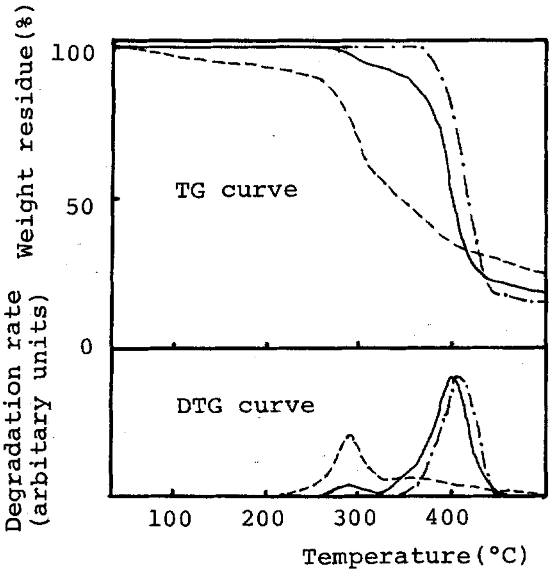


Fig. 3
TG and DTG curves of the fractionated polymers in the ALV/MA system (MA-2)
——— Insoluble part
- - - - MeOH-soluble part
—·—·· AcOEt-soluble part

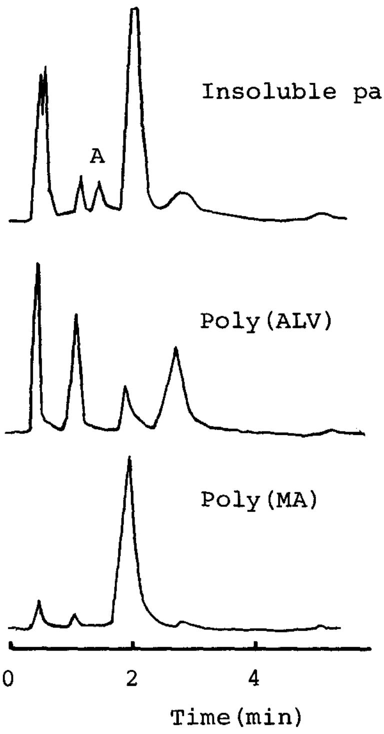


Fig. 4
Pyrograms of poly(ALV), poly(MA) and the insoluble part of the ALV/MA system (MA-1): pyrolysis temperature, 460°C; column(PEG 6000) temperature, 52°C

linkage between both sequences.

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