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Studies on diacetylenic vinyl compounds

IV. Copolymerization of phenyl-4'-vinylphenylbutadiyne with maleic anhydride

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ABSTRACT

The copolymerization of maleic anhydride(MAn) with phenyl-4'-vinylphenylbutadiyne(PVPB) was carried out using 2,2'-azobisisobutyronitrile as an initiator. Although PVPB does not homopolymerize by free radicals in solution, it copolymerized giving copolymers having average molecular weights up to 12,000, and consisting of slightly more PVPB units. The monomer reactivity ratios were estimated to be r(MAn)=0 and r(PVPB) =0.1 - 0.2. It was concluded that the copolymerization likely proceeds via a free monomer propagation mechanism rather than through a donor-acceptor complex mechanism.

INTRODUCTION

In order to obtain functional polymers, the present authors are studying synthesis of vinyl polymers containing acetylenic and diacetylenic groups. Previously phenyl-4'-vinyl phenylbutadiyne (PVPB) was synthesized, and its polymerization in the solid state was investigated(1,2). PVPB does not give polymer when polymerized in solution by free radicals due to the interaction of propagating radical with the diacetylenic group(1). However it copolymerizes with styrene and with methyl methacrylate to give PVPB rich copolymers(3). The copolymerization rates and the molecular weights of copolymers were much lower than those for the homopolymerization of styrene and the copolymerization of styrene with methylmethacrylate. When the concentration of PVPB is low; less than 5 mol% to the comonomer, the copolymerization is rapid and gelation took place as the viscosity of the system increased. The propagating radicals interact with the diacetylenic groups and this competes with the propagation. In fact such an interaction of propagating radicals with the diacetylenic groups was confirmed by the ESR spectroscopy(4). The free radical polymerization of vinyl monomers in the presence of diphenylbutadiyne(DPB) was also investigated(5). The retardation effect of DPB was prominent, and specially the polymerization of vinyl monomers which give secondary radicals with low Q values, such as acrylonitrile(AN), methylacrylate(MA) and vinyl acetate(VOAc), was drastically retarded.

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The copolymerization of maleic anhydride(MAn) with high electronic density vinyl monomers has been studied by many and the mechanisms of alternating copolymerization have been discussed extensively(6,7,8). It is expected that PVPB and MAn will give an alternating copolymer because PVPB is a styrene derivative. It is of interest also to observe the behavior of the diacetylenic group of PVPB in the copolymerization with MAn. In order to obtain information on the alternating copolymerization mechanisms of MAn, the copolymerization was carried out and the results are presented in this paper.

EXPERIMENTAL

(1) Materials:

PVBP was obtained from 2-chloroethylbenzene by the method reported previously (1). It was purified by repeated recrystallization from methanol before use. MAn was purified by sublimation. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

(2) Copolymerization:

Required amounts of PVPB, MAn, AIBN as a benzene solution and benzene were placed in a Pyrex tube, which was sealed off after repeated degassing by freeze and thaw process, and the tube was placed in a constant temperature bath with or without agitation. After the polymerization, the content was poured into dry ether, and the precipitated yellow copolymer was washed with dry ether, filtered and dried under vacuum.

(3) Characterization of Copolymer:

The NMR spectra of PVPB, MAn and their equimolar mixture were taken using a Bruker NMR spectrometer Model AC-80. The molecular weight was determined by GPC using a Waters Associates Liquid Chromatograph Model 501 with 2 columns of Ultra Styrogel PN 10 681 in tetrahydrofuran as a solvent. The elemental analysis of copolymers was done using a Carlo Erba Elemental Analyzer Model 1106.

RESULTS AND DISCUSSION

In order to see whether a charge transfer complex is formed between PVPB and MAn, 1-H and 13-C NMR spectra were taken and the results are summerized in Table 1. As can be seen in the table, the changes in chemical shifts of vinyl protons and vinyl carbons were very small. In the case of 13-C spectra, the change was almost negligible. The decreases in chemical shifts of MAn

TABLE 1. Chemical shifts of NMR spectra of PVPB, MAn and their equimolecular mixture.

Solvent	PVPB		MAn	PVPB-MAn mixture		
	$CH_2=$ *	=CH-*	-CH=CH-	$CH_2=$ *	=CH-*	-CH=CH-
C_6D_6(1-H)	6.236	4.960	5.853	6.260	4.992	5.673
$CDCl_3$(1-H)	6.510	5.218	7.068	6.500	5.213	6.905
$CDCl_3$(13-C)	115.38	126.30	136.38	115.50	126.35	136.31

*: Chemical shift of the peak at the lowest field among the four(quartet) peaks.

TABLE 2. Copolymerization of MAn(M_1) with PVPB(M_2).

No.	$[M_1]$mmol.	$[M_2]$mmol.	$[M_1]/[M_2]$	AIBNmmol	Benzene	T(°C)	Polym. Time(hr)	Yield (g)	(%)	MWt
1	4.208	1.053	3.996	0.06	3 ml	50	37.5	0.044	6.7	600
2	1.579	1.053	1.500	0.06	3 ml	50	37.5	0.023	5.7	1500
3	1.315	1.316	1.001	0.06	3 ml	50	19.0	0.014	3.2	1900
4	1.052	1.579	0.666	0.06	3 ml	50	37.5	0.014	3.0	1500
5	1.276	1.277	1.001	0.06	3 ml	55	24	0.107	23.5	--
6	1.188	1.187	0.999	0.06	3 ml	75	24	0.144	31.9	8000
7	3.949	1.316	3.000	0.03	1.5 ml	60	26	0.333	48.5	gel
8	2.632	1.316	2.000	0.03	1.5 ml	60	26	0.300	55.8	gel
9	1.315	1.316	0.999	0.03	1.5 ml	60	26	0.230	53.6	11250
10	0.987	1.316	0.750	0.03	1.5 ml	60	26	0.210	52.9	12530
11	0.658	1.316	0.500	0.03	1.5 ml	60	26	0.165	45.3	11250

TABLE 3. Composition of Copolymers.

No.	$[M_1]/[M_2]$	C %	H %	$d[M_1]/d[M_2]$
7	3.00	83.09	4.07	0.86
8	2.00	82.72	4.58	0.83
9	1.00	82.68	4.78	0.83
10	0.75	83.69	4.23	0.72
11	0.50	84.52	4.71	0.67

protons in d-benzene and in d-chloroform by mixing with PVPB were found to be o.167 and 0.179, respectively, indicating that MAn increased its electronic density by mixing. But those for PVPB protons were in the range of only 0.01 and 0.03 ppm. The distance between the peaks of different protons of PVPB did not change by mixing with MAn. UV spectra of the system were taken but no appreciable change in the peak positions was observed. No coloration was observed by mixing the two compounds. Furthermore little polymerization took place at 50°C in the absence of AIBN. From these observations it can be said that no charge transfer complex is formed in this system, although an interaction probably exists between the two.

Table 2 shows the results of copolymerization. Under the experimental conditions of this work, the polymer yield tends to decrease with increase in the PVPB concentration. Both MAn and PVPB do not give polymers when polymerized alone in solution with free radicals, but PVPB can copolymerize with some vinyl monomers such as styrene and methylmethacrylate(3) giving PVPB rich copolymers. The reason why PVPB can readily copolymerize, is that the relative concentration of diacetylenic group to the vinyl group decreases when a comonomer is added, and this increases the ratio of propagation reactions to the trapping of the propagating radicals by the diacetylenic groups. Consequently the polymerization yield increases with decrease in the diacetylene concentration; i.e. PVPB concentration.

Crosslinked copolymer was obtained in the case of No. 7 and No.8. This type of gelation was also observed for the copolymerization of PVPB with styrene and with methylmethacrylate, when the PVPB concentration was low(3). When the PVPB concentration is low the polymerization is rapid and the viscosity of the system increases, inhibiting the motion of propagating polymer chain radical which is trapped temporarily by the diacetylenic group, and the system suddenly becomes a gel. The system becomes pale green luminescent and at this point the system shows ESR signals(4).

Although sufficient data are not available, the monomer reactivity ratios were estimated using the Mayo-Lewis integrated equation(9). The values of r_1(MAn) and r_2(PVPB) were found to be 0 and 0.1 - 0.2, respectively. The monomer feed-copolymer composition curve is shown in Fig. 1, plotting the results shown in Table 3. It can be seen that PVPB-rich copolymers are obtained with a tendency of alternating copolymerization. PVPB should have a greater value of resonance stabilization, Q, than styrene, because the color of the anionic polymerization system of PVPB using n-butyllithium is deep blue, while that of styrene is red. The e value of PVPB is expected to be slightly less than that of styrene due to the acetylenic group. From the above comparison, such a deviation from ideal alternation, as shown in Fig. 1, can be expected.

The copolymerization of methylacrylate(MA) with PVPB was carried out under the same conditions for No.7 - 11 in Table 2. The yields were low being less than 10 % of those for MAn-PVPB system. As mentioned ealier, the polymerization of MA is considerably retarded by the addition of DPB. MA can homopolymerize very rapidly and it has a larger Q value(0.42) than MAn(0.23)(10). The relatively faster copolymerization of MAn-PVPB system compared to the MA-PVPB system is attributed to the

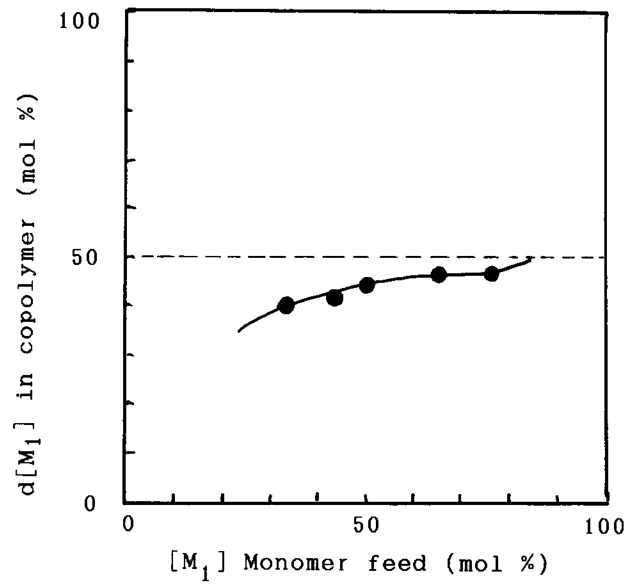

Fig. 1. Monomer-Copolymer Composition Curve. M_1 = MAn. From the data of Table 3.

polar effect in propagation step. Since MAn is a stronger electron acceptor monomer than MA, there exist in the MAn-PVPB copolymerization system, electrostatic interactions between the electron donor radical and electron acceptor monomer, and between the electron acceptor radical and electron donor monomer. This leads to a decrease in the activation energy for cross-propagation, and also to a decrease in the intraction or trapping of propagating radical with the diacetylenic group of PVPB.

In the cases of copolymerizations Nos. 1 - 4 in Table 2, the benzene used as a solvent was not dry, and MAn was partly hydrolyzed. This is probably why the yields were rather poor.

It can be concluded that the copolymerization of MAn with PVPB has an alternating character, and the propagation is the free monomer propagation with participation of polar effect, which decreases the trapping of propagating radicals by the diacetylenic group of PVPB. Charge transfer complex copolymerization is considered to be unlikely in this system.

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REFERENCES

(1) BURILLO, G. and OGAWA, T., Polym. Bulletin, 16, 257(1986)

(2) BURILLO, G., AGUIRRE, M. E. and OGAWA, T., Submitted for publication in this journal(Jan. 1989). Work presented at 32 nd Int. Symp. Macromolecules(MACRO 88), Aug. 1988, Kyoto, Japan.

(3) CASTILLON, F. F., NAVARRO, R. E. and OGAWA, T., J. Polym. Sci., Polym. Chem. Ed., 26, 321(1988)

(4) HWANG, J. S. and OGAWA, T. unpublished results.

(5) NAVARRO, R. E. and OGAWA, T., J. Polym. Sci., Polym. Chem. Ed., in press.

(6) TRIVEDI, B. C. and CULBERTSON, B. M., "Maleic Anhydride", Plenum Press, New York and London, 1982.

(7) RATZSCH, M., Prog. Polym. Sci., vol. 13, 277(1988).

(8) SEYMOUR, R. B., Arabian J. Sci. and Eng., 13, No.4, 600 (1988)

(9) MAYO, F. R. and LEWIS, F. M., J. Am. Chem. Soc., 66, 1594 (1944).

(10) YOUNG, L. J., "Tabulation of Q-e Values". pp387-403, in Chapt. II in "Polymer Handbook", BRUNDRUP, J. and IMMERGUT, E. H. with McDOWELL, W., Eds., Wiley-Interscience, New York !975.

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