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Free radical copolymerization of 4-phenylbut-1-en-3-yne with methylmethacrylate

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SUMMARY

Free radical copolymerization of 4-phenylbut-1-en-3-yne (PB) with methyl methacrylate(MMA) was studied. The polymerization of MMA was inhibited by the presence of small amounts of PB, but the copolymerization yield incresed with increase in the PB concentration, and PB-rich copolymers were obtained. The monomer reactivity ratios, r_{MMA} and r_{PB}, were found to be 0.096 and 2.83, respectively. The *Q* and *e* values of PB were calculated by using the values of MMA and were found to be 2.69 and 0.74, respectively. The slow polymerization and low molecular weights were attributed to the low propagating activity of PB radicals.

Introduction

Although conjugated enyne hydrocarbons are interesting monomers for synthesis of functional polymers, very little has been studied in recent years. This is prbably because of early studies1) which have shown that vinyl acetylene does not give useful high polymers and other vinyl acetylenes mainly undergo cyclization instead of polymerization. Therefore vinyl acetylenes are thought to have little value as monomers for commercial polymers.

The present authors are interested in the polymerization of conjugated enynes, in particular the effects of the conjugated double or triple bond on the polymerizability of the terminal unsaturated group, as well as in the structures of the polymers obtained. Previously, the polymerization of 2-methyl-4-phenylbut-1-en-3-yne was investigated using free radical, anionic and cationic initiators2), and it was found that the monomer undergoes ionic polymerization with n-butyl lithium or boron trifluoride etherate, giving a linear polymer, and that no free radical polymerization took place in solution but thermal polymerization occurred when heated to 120°C in the absence of initiator. These polymers were found to crosslink when heated through the remaining acetylenic bonds.

Very little is known about copolymerization of vinyl acetylenes with other monomers. Vinyl acetylene is said to retard the free radical polymerization of vinyl

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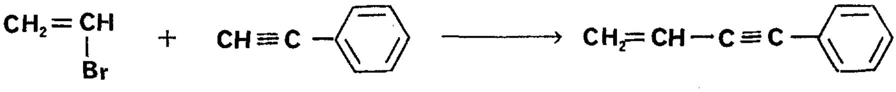
acetate[3)] and chloroprene[4)]. In this work 4-phenyl-but-1-en-3-yne (PB) was prepared and its free radical copolymerization with MMA was investigated.

Experimental.

Synthesis of PB.

PB was synthesized using the Heck reaction of vinyl bromide with phenyl acetylene:



30 g of freshly distilled phenyl acetylene, 30 g of vinyl bromide (both supplied by Aldrich) 0.3g each of triphenylphosphine and copper(I) iodide, 200 ml each of pyridine and triethylamine, were placed in a high pressure reactor(Parr Ser.4560, 600ml). After purging the air in the system by passing nitrogen, 0.3 g of bistriphenylphosphine palladium dichloride was added, and the mixture was heated to 50°C. The temperature of the system rose to about 100°C and the system was cooled by circulating water. After about 5 hrs of reaction, the precipitated triethylmine hydrobromide was filtered, and washed with triethylamine. The mother liquors were combined, and pyridine and triethylamine were evaporated under reduced pressure. The remaining product was then distilled under vacuum, and a colorless liquid boiling at 35°C was collected. The yield was about 60 %. The product was redistilled twice under reduced pressure before polymerization.

Copolymerization.

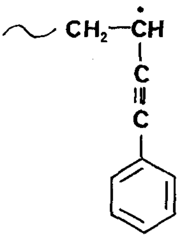
Required amounts of freshly distilled MMA and PB were placed in Pyrex ampoules and after repeated freezing and melt degassing the ampoules were sealed under vacuum, and heated at 60°C for 41 hours. The pale yellow polymers formed were precipitated in methanol, filtered, washed well with methanol, and dried under vacuum at room temperature.

Characterization

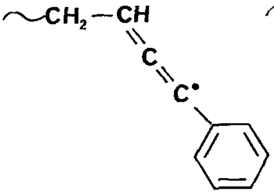
The average molecular weights of the copolymers were determined by GPC(Varian Model 9012 with a detector RI-4, integrator 4400 and a column with polystyrene, Type G5000HXL) at room temperature using tetrahydrofuran as a solvent. The ^1H NMR spectrum of PB was taken with a JEOL PMX60 spectrometer, and ^1H and ^{13}C NMR spectra of polyPBs were taken by using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively. $CDCl_3$ was used as solvent. IR spectra of polyPBs were taken by using a Nicolet 510P FT-IR spectrometer. The copolymer compositions were determined by elemental analysis carried out by Desert Analytics of Tucson, AZ, USA.

Results and Discussion.

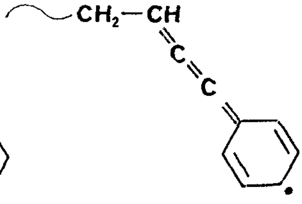
As can be seen from Table 1 and Fig.1, no methanol-insoluble product was isolated with PB concentration less than about 10 mole % under the conditions of this work, and the yields increased with increasing PB concentrations. Copolymerizations were repeated three times, and the results were found to be very well reproducible. These results suggest that MMA radicals add to PB and the resulting PB radicals are poorly capable of adding to MMA, or that PB interacts with MMA radicals forming unreactive species. Radical **I** may change to radicals **II** and **III** which are more stable than **I** however no evidence of the formation of **II** and **III** is available.



I



II



III.

Table 1. Copolymerization of PB with MMA at 60°C for 41 hours.

Run	PB (m mol)	MMA (m Mol)	$[PB]_0$ (mol %)	Yield[a] (%)	d[PB] (mol %)	M_w	M_n
1	0	37.20	0	100	----	----	----
2	2.93	33.58	8.04	0	----	----	----
3	5.87	29.76	16.14	0.50	49.0	----	----
4	8.81	26.04	25.27	1.77	60.0	5200	1400
5	11.75	22.32	34.48	3.27	68.0	6100	1600
6	14.68	18.60	44.11	4.04	74.5	6500	2000
7	17.62	14.88	54.21	5.51	82.0	6600	2030
8	20.56	11.16	64.81	7.91	84.0	7200	2550
9	23.50	7.44	75.95	10.07	91.0	6900	2600
10	26.43	3.72	87.66	12.42	94.0	8550	3470
11	29.37	0	100	15.60	----	9240	3560

$[PB]_0$ = initial feed, d[PB] = in copolymer.

a : Based on the total weight of monomers.

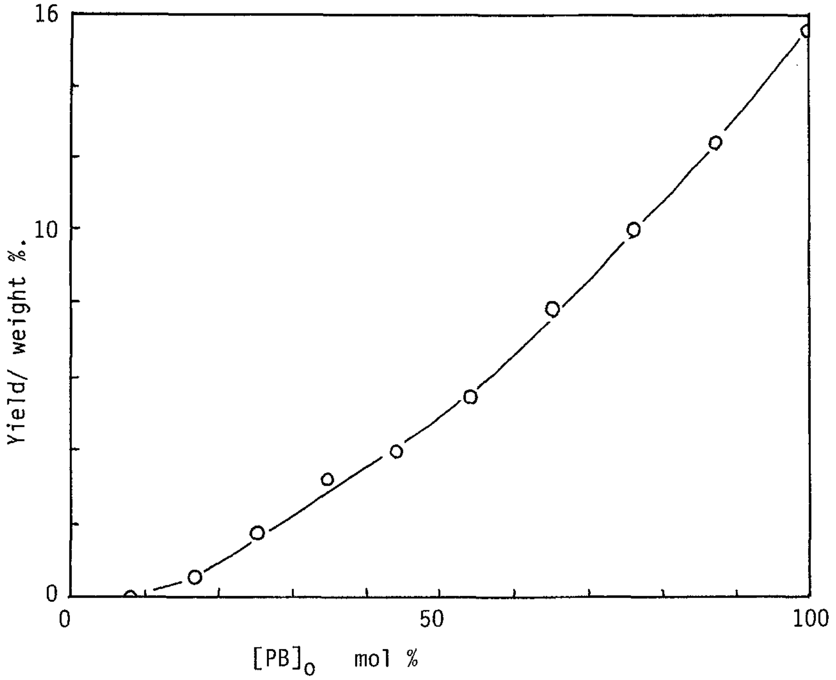


Fig. 1. The relationship between the initial concentration of PB and polymerization yields. 60°C for 41 hrs.

^{1}H NMR spectra(Fig. 2) and IR spectra of copolymers showed that the double bond of PB was used for polymerization. Both ^{13}C and ^{1}H NMR specta of the polyPBs obtained both by thermal polymerization at 120°C and by AIBN-initiated homopolymerization at 60°C, were taken but no evidence for the formation of allenic(II) or quinolic(III) structures was observed, and therefore the polymerization of PB is considered to be a 1,2-polymerization.

The copolymer composition curve is shown in Fig.3, which demonstrates that PB is incorporated predominantly. The monomer reactivity ratios, $r_{1(PB)}$ and $r_{2(MMA)}$ were calculated from the data shown in Table 1(excluding Run 11), using the Fineman-Ross method(Fig.4), and they were found to be 2.83 and 0.096, respectively. The Q and e values of PB were calculated using the known Q and e values of of MMA$^{4)}$, and found to be 2.69 and 0.74, respectively. The Q value seems to be very high for a secondary radical, even higher than that of butadiene(Q=2.39)$^{5)}$. The UV absorption spectrum of PB was taken in ethanol. It had an absorption maximum, λ_{max}, due to the π-π^* transition of CC double bond at 220 nm. Ito et al.$^{6)}$ have shown that a linear relationship exists between *log*Q and the λ_{max} for about 30 vinyl monomers. The plot of *log*Q_1(0.43) against 220 nm was found to be very agreeable with the above study indicating that the value of Q_1 found for PB in this study is correct. The e value appears to be reasonable considering the nature of phenylethynyl group. The extremely low rate of polymerization is probably due to the very small propagation rate constant of PB, as commonly observed for most high Q value monomers, such as isoprene(Q=3.33, k_p= 2.8 l mol^{-1} sec^{-1} at 5°C) and butadiene(Q=2.39, k_p= 8.4 l mol^{-1} sec^{-1})(5). The low molecular weights of these copolymers, shown in Table 1, can also be attributed to the low rate of propagation of PB.

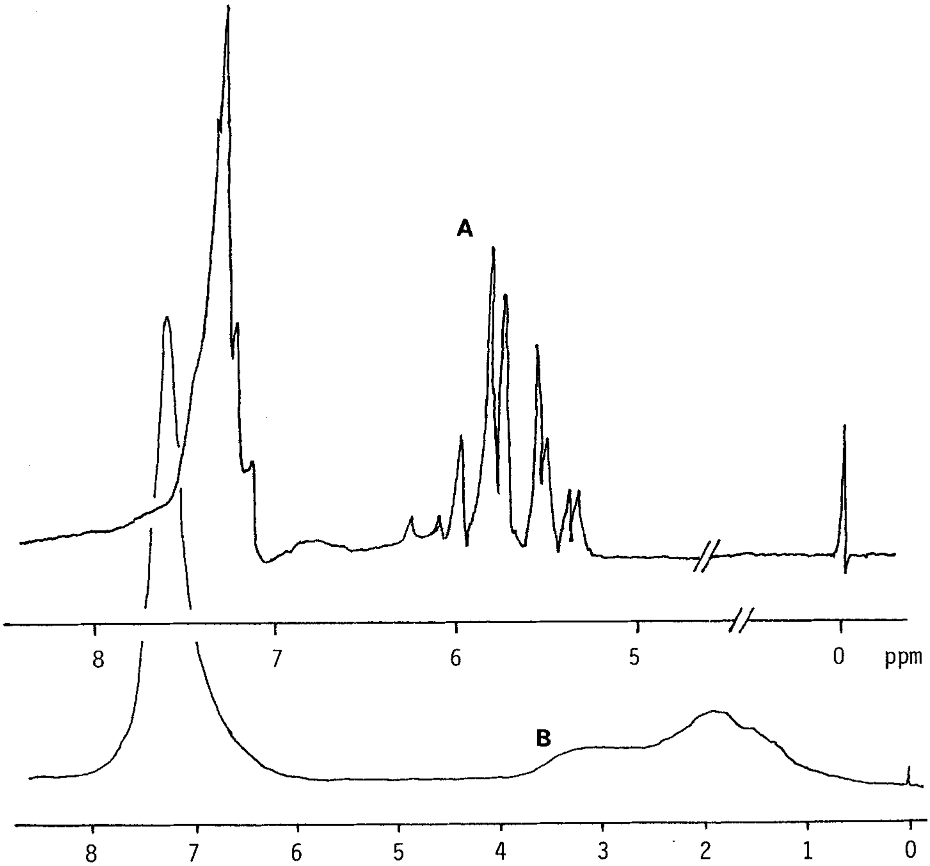


Fig. 2. ^{1}H NMR sepctra of PB(A) and polyPB(b).

In the case of 2-methyl-4-phenylbut-1-en-3-yne(2), MPB, no polymerization took place in solution using AIBN as initiator, but it gave a vinyl polymer when heated in bulk at 120°C without initiator. Thermal dimerization and subsequent ring-opening mechanism was proposed for this polymerization(2). Under the copolymerization conditions of this work, i.e., in benzene at 60°C, such dimerization probably will not takes place. It was found that the polymerization of PB did not take place at 60° C without AIBN, and therefore the radical from AIBN adds to PB to form radical **I**, which then enters propagation.

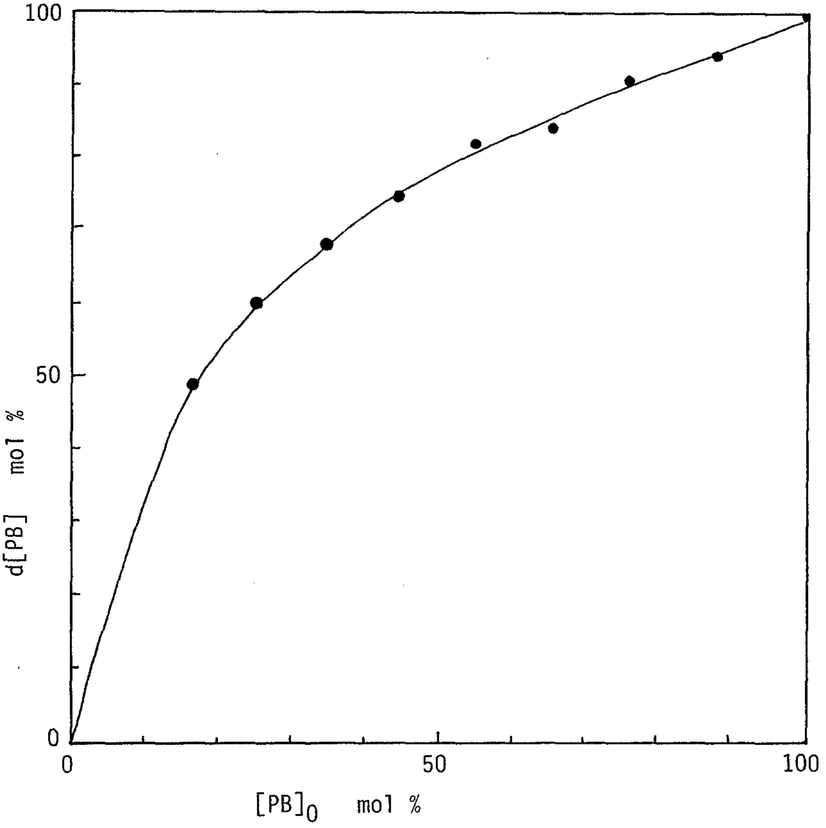


Fig. 3. The copolymer composition curve.

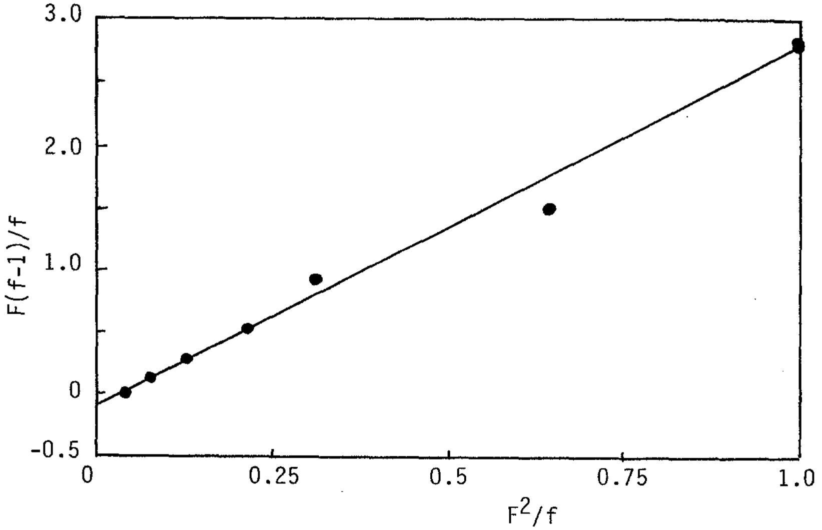


Fig. 4. Fineman-Ross plot of copolymerization of PB with MMA.

When PB was heated to 120°C in a sealed tube without solvent and initiator, it polymerized rapidly, and a 90% conversion was achieved within 6 hrs. The molecular weight, Mn, was found to be 1500. IR spectra of this polymer and that of polyPB obtained in benzene solution with AIBN were identical.

From these results it is concluded that PB and MPB form rather stable propagating radicals (low k_p) and thus give low molecular weight polymers. It is interesting to note that the acetylenic groups on the vinyl bonds affect very significantly the free radical polymerizability of the vinyl monomers.

PB underwent anionic polymerization at room temperature using tetrahydrofuran as solvent and n-butyllithium as initiator. The IR and ^{1}H NMR spectra of the polyPB obtained were same as those of a polyPB obtained by free radical polymerization.

Aknowledgement

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