Polymer Bulletin 6, 217–223 (1981)

Polymer Bulletin

Electrochemically Initiated Copolymerization of some Acetylenic Derivatives

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SUMMARY

Electrochemically initiated copolymerization of some donor and acceptor acetylenic monomers (phenylacetylene and diphenyldiacetylene as donors and methyl propiolate as acceptor) was studied.

INTRODUCTION

The obtaining of macromolecular compounds by electrochemical initiation is a new method of polymer, copolymer and polycondensation precursors synthesis.
In some previously published papers (FARAFONOV et al., 1977; SIMIONESCU et al., 1978; 1979) the electrochemically initiated polymerization of phenylacetylene, diphenyldiacetylene and of methyl propiolate was reported. SUBRAMANIAN et al. (1978a) also published some data on the polymerization of phenylacetylene, as well as on the copolymerization of phenylacetylene with benzonitrile (SUBRAMANIAN et al., 1978b; JAKUBOWSKI and SUBRAMANIAN, 1979). All these results proved the existence of an anionic mechanism of polymerization.
The copolymerization of acetylenic monomers has already been performed with radical initiators, cationic catalysts, Ziegler-Natta homogeneous and heterogeneous catalysts, and with catalytic systems consisting of compounds of VIII-th group transitional metals and of hidrides of the I-IV group elements (CHAUSER et al., 1976; BULACOVSCHI and SIMIONESCU, 1975).
An unconventional method - the copolycyclotrimerization and the copolycyclodimerization of mono- and diacetylenes - led to copolymers with unexpected thermomechanical properties (SERGEEV et al., 1980; LEBEDEV et al., 1980).
The peculiarity of direct electrochemical initiation of the copolymerization process appears from the fact that, for a given potential, one of the monomers becomes initiator of the reaction.
The present paper deals with the electrochemically

0170-0839/81/0006/0217/$01.40

initiated copolymerization of phenylacetylene (PhA) and of diphenyldiacetylene (DPhDA) with methyl propiolate (MP). The reactions were performed in dimethylformamide (DMF), using alkyl ammonium perchlorates as support electrolytes - $(R_4N)ClO_4$ (R: $-CH_3$, $-C_2H_5$, $-C_4H_9$).

EXPERIMENTAL

PhA (FOREST, 1964), DPhDA (Serva) (HAY, 1960), MP (MOUREU and BONGRAND, 1920) and $(R_4N)ClO_4$ (OLAJ et al., 1968) were prepared and purified according to literature methods. DMF (Fluka), of high purity, was refluxed and vacuum distilled (JUILLARD, 1977).
The apparatus used and the working procedure were previously described (SIMIONESCU et al., 1979).
The separation of the copolymers from the reaction mixture was performed mainly as follows:
The reaction mixture was poured into a large excess of diluted HCl aqueous solution, and the copolymer was extracted with chloroform; the chloroform solution was then washed with water, dried on anhydrous Na_2SO_4 and evaporated up to about 1/20 from its volume.
The remaining chloroform solution was poured into a large amount of hexane to precipitate the PhA-MP copolymer which was then filtrated and dried.
As concerns the DPhDA-MP copolymer, the product was isolated in the same manner; the copolymer was extracted in a Soxhlet apparatus, with petroleum ether, in order to remove the unreacted DPhDA.
Copolymer composition was established from elementary analysis data and NMR spectra (registered on a Jeol-C60 HL apparatus, in $CDCl_3$). IR spectra were registered on a Perkin-Elmer spectrometer (KBr pellets); the melting points were determined with a Boetius microscope. ESR spectra were registered on a EPR-Spectrometer-Art. 5 - IFA. The viscosities were measured with an Ostwald viscometer, in acetone, at 20° C.

RESULTS AND DISCUSSION

The polymerization reaction took place only in the cathodic compartment. Table 1 summarizes the copolymerization conditions.
As it can be seen, the best yield was obtained using $(C_4H_9)_4NClO_4$ as electrolyte. This experimental observation can be explained by the increase of the dissociation constant of the macroanion-tetraalkyl ammonium cation ion pair with the increase of cation radius, and also taking into account the solvent characteristics (ε=35, donor number =30.9).
Monomer/electrolyte molar ratio was 23.1:1 for PhA-MP copolymer, and 16:1 for DPhDA-MP copolymer.
Table 2 presents the influence of molar ratios of the

reagents on the copolymerization process, for systems using as electrolyte $(CH_3)_4NClO_4$.

TABLE 1
Electroinitiated copolymerization of MP with PhA and with DPhDA

Sample	MP mol·l^{-1}	Donor monomer D	mol %	Electrolyte mol·l^{-1}	Yield %
1	0.8	PhA	50	$(CH_3)_4NClO_4$ 0.075	23.4
2	0.8	PhA	50	$(C_2H_5)_4NClO_4$ 0.075	32.0
3	0.8	PhA	50	$(C_4H_9)_4NClO_4$ 0.075	48.7
4	0.8	DPhDA	33	$(CH_3)_4NClO_4$ 0.075	53.4
5	0.8	DPhDA	33	$(C_2H_5)_4NClO_4$ 0.075	49.1
6	0.8	DPhDA	33	$(C_4H_9)_4NClO_4$ 0.075	61.3

Initial current = 30 mA; T = 10° C; duration = 5 h.

TABLE 2
Influence of molar ratios of reagents on electroinitiated copolymerization of some acetylenic monomers

Sample	Donor	mol·l^{-1}	MP mol·l^{-1}	D / A	Molar ratio monomer/ electrolyte	Yield %
1	PhA	1.2	0.4	3:1	21.33/1	55.76
2	PhA	0.8	0.8	1:1	21.33/1	23.41
3	PhA	0.4	1.2	1:3	21.33/1	20.21
4	DPhDA	0.6	0.4	3:2	13.33/1	43.85
5	DPhDA	0.4	0.8	1:2	16.00/1	53.40
6	DPhDA	0.2	1.2	1:6	18.66/1	77.25

Initial current = 30 mA; T = 10° C; duration = 5 h.

For the same monomer/electrolyte molar ratio in the initial feed, the best yield, in the case of PhA-MP copolymers, was obtained for an excess of the donor monomer, and in the case of DPhDA-MP copolymers, for an excess of the acceptor monomer and for a less important concentration of the support electrolyte.
This behaviour could be due to the chemical structure of the donor components, as well as to their diffusion capacity from the cathode surface into the volume of the solution.
The composition of the copolymers and some characteristics are presented in Table 3.
From the point of view of composition, all the copolymers, for initially equal molar ratio, are richer in

the acceptor compound, phenomenon also observed in the radical copolymerization of PhA with MP. The copolymer composition, determined by NMR spectroscopy, was in agreement with that established from elemental analyses data.

FURUKAWA et al. (1980) synthetized almost 1:1 copolymers starting from acetylenic donors and acceptors, using $EtAlCl_2$ type catalytic systems with or without compounds of transitional metals.

SHCHERBINA (1979) obtained paramagnetic products from the copolymerization of propiolic acid with PhA, by γrays initiation; the copolymer yield was little affected by changes in initial monomer ratio (1:2 - 2:1) in the reaction mixture.

TABLE 3

Copolymer composition and some characteristics

Sample	D, mol % feed/copol.	Elementary anal. calc.*		exptl.		Aspect	Melting point, °C
		C	H	C	H		
Phenylacetylene							
1	75/21.89	66.53	5.05	64.08	5.57	b	125-170
2	50/13.40	62.99	4.94	60.16	4.99	d-b	164-195
3	25/11.18	62.05	4.91	59.87	5.30	y-b	134-154
Diphenyldiacetylene							
4	60/36.39	79.09	4.87	70.68	5.03	d-b	142-156
5	33.3/19.94	71.34	4.83	65.93	4.95	y-b	138-162
6	14.3/18.83	70.72	4.83	68.43	5.29	b	96-112

*composition calculated from the initial feed

b - brown; d-b - dark brown; y-b - yellow brown.

In the case of electrochemical copolymerization, the monomers ratio in the initial mixture modifies both the yield and the copolymer composition, this being an advantage of the method.

Typical NMR spectra of PhA-MP and DPhDA-MP copolymers are presented in Figure 1. PhA-MP copolymers show the following NMR signals: δ = 6.9-7.5 ppm, attributed to olefinic and aromatic protons, δ = 2.8-4.3 ppm, due to methyl protons from the esteric group, and DPhDA-MP copolymers present signals at δ = 6.4-7.6 ppm, due to olefinic and aromatic protons and δ = 3.1-4.0 ppm for the methyl protons in esteric group.

IR spectra of the copolymers are presented in Figure 2 and in Figure 3. The electrolyte has no influence on copolymer structure. In Figure 2 (PhA-MP copolymers) one can see the C=O group peak from the ester at 1700 cm^{-1}, the absorption due to C=C conjugated bond at 1640 cm^{-1}, and the absorption of phenyl group at 700 and 765 cm^{-1}. The specific absorption of $C\equiv C$ bond at 2100 cm^{-1} was not identified. IR spectra don't allow the obtaining of data on the microstructure of the copolymers, due to the unsaturation of the main chain.

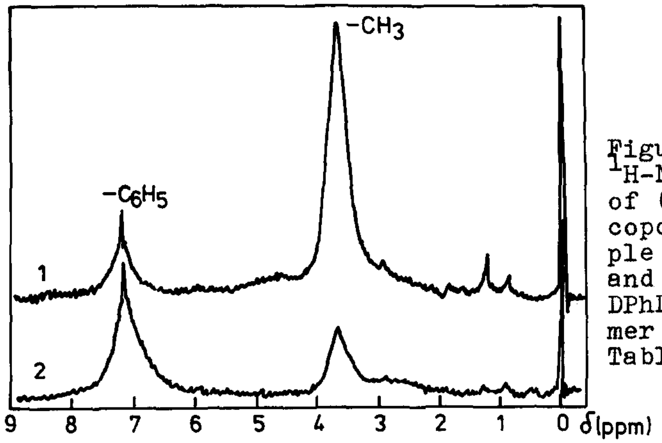

Figure 1. ^{1}H-NMR spectra of (1) PhA-MP copolymer (sample 2, Table 2) and of (2) DPhDA-MP copolymer (sample 4, Table 2).

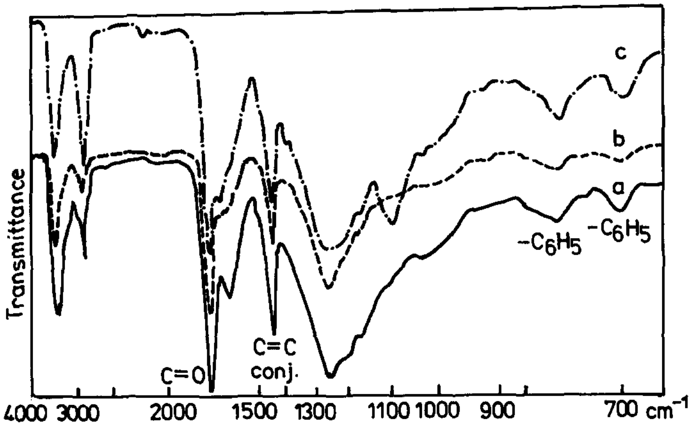

Figure 2. IR spectra of PhA-MP copolymers obtained with alkyl ammonium perchlorates as support electrolytes: (a) $(CH_3)_4NClO_4$; (b) $(C_2H_5)_4NClO_4$; (c) $(C_4H_9)_4NClO_4$.

Figure 3 presents IR spectra DPhDA-MP copolymers obtained by using some alkyl ammonium electrolytes. Among with the specific absorptions, due to the presence of the esteric group and to the C=C bond, already presented, the aromatic compound is identified by the following characteristic absorption: 700 and 755 cm^{-1} (out-of-plane deformation vibrations of C-H bond from the monosubstituted C_6H_6), 1440 and 1490 cm^{-1} (vibrations of the C=C bond from the aromatic nucleus).

The presence of two C≡C triple bonds in DPhDA makes possible the existence of more structures (MISIN et al., 1976).For DPhDA, the 1-4 bond is excluded, due

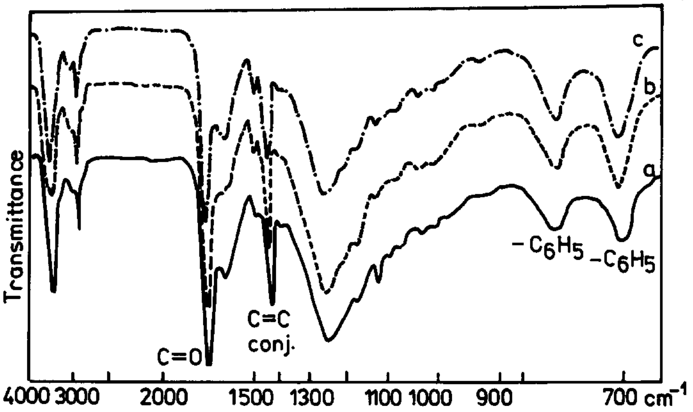

Figure 3. IR spectra of DPhDA-MP copolymers obtained with alkyl ammonium perchlorates as support electrolytes: (a) $(CH_3)_4NClO_4$; (b) $(C_2H_5)_4NClO_4$; (c) $(C_4H_9)_4NClO_4$.

to the absence of an absorption at 1950 cm^{-1}, specific for cumulenes. The individualization of a certain structure by IR spectroscopy is not possible, due to the symmetry of the substituents at the C=C and C≡C bonds.

The molecular weight of the obtained copolymers is low. Intrinsic viscosities were determined to be 0.067-0.087 dl/g.

The PhA-MP and DPhDA-MP copolymers were proved to be paramagnetic compounds, with 10^{17}-10^{18} spin/g concentration, depending on the content of the aromatic monomer in the copolymer.

The resistivity of copolymer pellets was measured in air and gave $\rho_{PhA-MP} = 2.26\cdot10^{15}$ and $\rho_{DPhDA-MP} = 1.69\cdot10^{12}$ ohm·cm.

Further research will be published in the near future.

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Received November 2o, accepted November 24, 1981