Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Free-Radical Polymerization of Dicyanoacetylene*

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To cite this Article Byrd, N. R. , Kleist, F. D. and Rembaum, A.(1967) 'Free-Radical Polymerization of Dicyanoacetylene*', Journal of Macromolecular Science, Part A, 1: 4, 627 — 633

To link to this Article: DOI: 10.1080/10601326708053999

URL: http://dx.doi.org/10.1080/10601326708053999

J. MACROMOL. SCI. (CHEM.), A1(4), 627–633 (1967)

Free-Radical Polymerization of Dicyanoacetylene*

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Summary

Dicyanoacetylene has been homopolymerized and copolymerized with styrene by a free-radical initiator. The homopolymerization was difficult to effect, but the copolymerization proceeded very well, to essentially a quantitative yield. Proof of the existence of a true copolymer was obtained by means of solubility tests and infrared spectroscopy. In addition, the reactivity ratios were calculated by means of infrared spectroscopy and it was found that the r_1 and r_2 values for styrene and dicyanoacetylene were 1.40 and approximately zero, respectively.

INTRODUCTION

Dicyanoacetylene (DCA) has been known for over 40 years, but it has been scantily investigated during that time. The most thorough research into its preparation, characterization, and reactions was that of Moureu and Bongrand (*1*). Subsequent to their work, other investigators examined the reactions (*2–4*), combustion (*5*). structures (*6*), and spectral properties (*7–9*) of DCA, but in each instance the method of preparation was almost identical to that

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[*] This work was performed under Contract NAS-7-100 to the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration.

described by Moureu and Bongrand (*1*). Recently, the polymerization characteristics of DCA were examined with the intent of obtaining a semiconducting polymer (*10*). However, only anionic polymerizations were studied, and no mention has been made in the literature about the free-radical polymerizability of DCA.

The present paper describes the free radical–initiated homopolymerization and copolymerization of dicyanoacetylene, which has not heretofore been reported.

EXPERIMENTAL*

Acetylenedicarboxamide (I)

The method used was a slight modification of that reported by Blomquist and Winslow (2) and by Moureu and Bongrand (*1*). To 80 ml of concentrated NH_4OH, dissolved in 100 ml of ethanol and cooled to −19°C, was added 20 g of acetylenedicarboxylic acid dimethylester (Gallard-Schlesinger Chemical Mfg. Co.) dissolved in 100 ml of ethanol. The addition was dropwise with vigorous stirring while maintaining the temperature around −14°C. Upon completion of the addition, the temperature was allowed to rise to 15°C, and the slurry filtered, washed with water until washings were neutral to pH paper, and finally washed with alcohol. The powder was dried in a vacuum desiccator for 24 hr, yielding 13 g (83%) of I, melting point 195°C (dec.) Reported m.p. 290 to 292°C (2). *Analysis:* Theoretical: C, 42.85%; H, 3.59%; N, 24.98%. Found: C, 42.86%; H, 3.75%; N, 25.04%.

Acetylenedicarbonitrile (DCA) (II)

A modification of the Moureau and Bongrand procedure was used (*1*). A mixture of 100 g of washed and ignited sand, 50 g of P_2O_5 and 6 g of I was prepared in a 1000-ml long-neck, ₸ 24/40, round-bottom flask. At the end of the neck, near the standard taper joint, was placed a plug of glass wool and the flask attached to a rotating evaporator (Rinco-Vac). The takeoff from the evaporator was connected with rubber tubing to a vacuum system. The entire system was evacuated to 10 μ, and a bath, heated to 215°C, was

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* Elemental analyses by Elek Microanalytical Laboratories, Los Angeles, Calif. All melting points are uncorrected.

brought into sudden contact with the rotating flask containing the reactants. At the same time, the first receiver, as well as the trap, in the vacuum line, were immersed in liquid nitrogen. Within 1 min after immersion in the heated bath, the product began to collect in the first receiver and the pressure began to rise. The reaction was allowed to continue until the pressure dropped to about 30 μ (usually about 30 min). At this point the heat was removed and the flask and pump were isolated from the system. The liquid nitrogen was removed from both the trap and the first receiver, and was placed around an ampoule which was located between the trap and the first receiver. When all collected, the system was evacuated to 10 μ and the ampoule sealed off. Yield was 1.65 g (40.7%).

Polymerization Studies

The following is representative of the radical-catalyzed polymerizations performed. All work was done under high vacuum on a vacuum rack. Into a 25-ml-capacity polymerization tube was placed 31 mg of azo-bis-isobutyronitrile (E. I. duPont de Nemours & Co.). This was attached to the vacuum rack and 3 ml of DCA was distilled into it under vacuum. To this was added 6 ml of tetrahydrofuran (which had been stored over Na-K alloy under vacuum), and 3 ml of styrene monomer, each distilled separately under vacuum. The polymerization tube was evacuated to 1×10^{-5} mm Hg and sealed off. It was placed in a 55°C oven for 21 hr, and when removed there was found to be a clear, deep brown solution. The ampoule was opened and the polymer precipitated into hexane to recover 5.27 g (97% yield) of a dark gray powder.

Other polymerizations carried out in a similar manner involved different volumes of monomers and different periods of time.

Extraction of Polymer

The 1:1 styrene/DCA copolymer (3.7728 g) was placed in a soxhlet thimble and extracted first with water for 48 hr. This was followed by extractions with methanol for 48 hr, toluene for 43 hr, and finally with acetone for 21 hr. The various solvents were evaporated to obtain the fraction of material soluble in each solvent. The total material balance gave a recovery value of 3.7660 g (0.0068 g loss in handling).

DISCUSSION AND RESULTS

Although the preparation and reactions of dicyanoacetylene have been discussed previously (*1–4*), prior to the work of Benes et al. (*10*), little information exists regarding its polymerization behavior. We have attempted to examine the radical-initiated homopolymerization and copolymerization of dicyanoacetylene.

Radical-initiated bulk homopolymerization of DCA does not occur readily. At the end of 1400 hr, only 7% of a brown polymer was obtained. However, in a 1:1 (volume ratio) DCA–styrene mixture, in tetrahydrofuran solution, there resulted a 97% conversion to a dark gray polymer at the end of 21 hours. Table 1 depicts the effect of solvent on the rate of total polymer formation. Without styrene present, the amount of polymer is also negligible.

We have observed, as have others (*10*), that polydicyanoacetylene is soluble in cold methanol or cold water, but is insoluble in toluene. A series of extractions was performed on the polymerization product to prove the formation of a true copolymer and not a mixture of homopolymers. Table 2 describes the extraction data. Cold water had little effect on the polymer, but hot water gradually removed a portion of the material. Similar results were found for the methanol-extraction process. The infrared spectrum of each fraction showed an almost identical spectrum, with DCA and styrene moieties being

TABLE 1

Solvent Effects on Total Polymer Formation at 55°C

Run	Monomers, ml	Solvent, ml	Time, hr	Catalyst,[a] g	Pressure in tube,[b] mm Hg	Yield	Remarks
1	DCA (2.6) Styrene (2.8)	Toluene (5.0)	17.5	0.025	8×10^{-5}	4.49 g (92%)	Pasty black material
2	DCA (3) Styrene (3)	THF (6)	21	0.031	9×10^{-5}	5.27 g (97%)	Dark grey powder
3	DCA (3.5) Styrene (3.5)	THF (5)	16	0.031	1×10^{-6}	5.442 g (85%)	Black material
4	DCA (2) Styrene (2)	Acetone (6)	23	0.032	1×10^{-5}	2.8835 g (80%)	Slightly sticky brown material
5	DCA (1.5)	None	18	0.018	1×10^{-5}	—	Traces of polymer
6	DCA (2.6)	None	1397	0.041	1×10^{-5}	0.1728 g	Dark brown solid, insoluble in H_2O, soluble in methanol

[a] Catalyst used was azo-bis-isobutyronitrile.

[b] Sealed-tube polymerizations.

TABLE 2

Extraction of DCA/Styrene (1:1) Copolymer

Time	Solvent	Weight of sample collected, g after removal of solvent[a]	Remarks
17 hr 30 min	H_2O	0.34619	Clear, dark brown solution when hot but cloudy when cool
7 hr 10 min	H_2O	0.04925	
16 hr 15 min	H_2O	0.08685	
7 hr 15 min	H_2O	0.0421	
48 hr 10 min		0.5244	
16 hr 25 min	MeOH	1.34805	A dark brown, slightly turbid solution when hot but very muddy looking when cool
7 hr 20 min	MeOH	0.7250	
15 hr 40 min	MeOH	0.28386	
8 hr 15 min	MeOH	0.1526	
47 hr 40 min		2.50951	
3 hr 45 min	Toluene	0.16182	A seemingly clear light brown (possibly colloidal) solution when hot but with some particles settling out when cool
17 hr	Toluene	0.3447	
6 hr 40 min	Toluene	0.04525	
15 hr 40 min	Toluene	0.0670	
43 hr 5 min		0.61877	
21 hr	Acetone	0.11328	Clear brown solution
159 hr 55 min		3.76596	

[a] Starting sample weight, 3.7728 g; recovered weight, 3.7660 g; loss in weight, 0.0068 g.

found in each sample: absorption at 4.5 μ for the cyano group and 13.1 and 14.25 μ for a monosubstituted phenyl group. This showed quite conclusively that we had a true copolymer.

To calculate the r_1 or r_2 values, polymerization of varying ratios of DCA/styrene were carried out to low conversions (approximately 10%). Attempts at obtaining elemental analyses proved fruitless, since no reproducibility could be obtained in the nitrogen determination. In view of this, infrared spectroscopy was used as a means of analysis, and it was found that regardless of the initial starting ratio there was always about 80% styrene in the copolymer. Thus, on the basis of the infrared analysis, the calculated r_1 and r_2 values for styrene and dicyanoacetylene were 1.40 for styrene and approximately zero for DCA. See Table 3 for analytical data.

TABLE 3

Per Cent Styrene in Polymer vs. Starting Monomer Mixture

Run	Monomer ratios (volume basis) DCA/styrene	Time, hr	Styrene,[a] %
1	50/50	2	79
2	50/50	4	71
3	50/50	6	80
4	50/50	21	75
5	40/60	2	55
6	50/50	2	73
7	75/25	2	80
8	80/20	2	86
9	90/10	2	91

[a] Determined by means of infrared spectroscopy.

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Received by editor October 3, 1966
Submitted for publication March 17, 1967

Zusammenfassung

Dicyanoacetylen wurde homopolymerisiert und mit Styrol in Gegenwart eines Radikalinitiators copolymerisiert. Die Homopolymerisation war schwierig durchzuführen, während die Copolymerisation sehr gut vor sich ging und zu im wesentlichen quantitativen Ausbeuten führte. Der Beweis für die Existenz eines wahren Copolymeren wurde durch Lösungsversuche und IR erbracht. Ausserdem wurden noch mittels IR Spektroskopie die Reaktivitätsverhältnisse berechnet und es wurde gefunden, dass die r_1 und r_2 Werte für Styrol und Dicyanoacetylen 1.40 und null sind.

Résumé

Le dicyanoacétylène a été homopolymérisé et copolymérisé avec le styrène par un initiateur radicalaire libre. L'homopolymérisation était difficile à effectuer, mais la copolymérisation proceda très bien avec un rendement essentiellement qualitatif. La preuve de l'existence d'un copolymère vrai a été obtenue à l'aide des tests de solubilité et de la spectroscopie infrarouge. On a aussi calculé les rapports de réactiviteé à l'aide de la spectroscopie infrarouge et on a trouvé que les valeurs r_1 et r_2 pour le styrène et le dicyanoacétylène étaient 1.40 et environ zéro respéctivement.