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Initiators

Initiating Carbenium Ions from Tetramethylene Zwitterions

Cationic Polymerizations Initiated by 2,2-Dicyanovinyl Iodide and 2,2-Dicyanovinyl p-Toluenesulfonate

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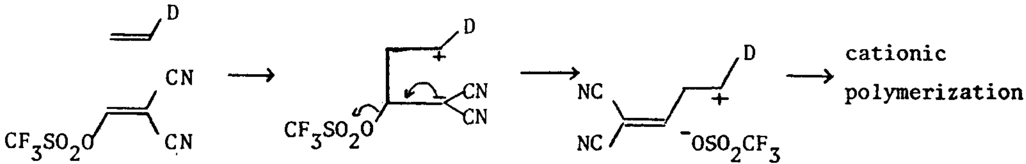
Abstract

Two new electrophilic olefins with a β-leaving group, 2,2-dicyanovinyl iodide and 2,2-dicyanovinyl p-toluenesulfonate initiate the cationic polymerization of N-vinylcarbazole and p-methoxystyrene. The polymerization of N-vinylcarbazole proceeds in the presence of the proton trap 2,4,6-tri-t-butylpyridine, indicating that the initiation proceeds through the zwitterionic tetramethylene, with subsequent elimination of the leaving group to form the initiating carbenium ion. No living character was observed with the iodide initiator.

Introduction

In our continuing research of the reactions of electron-poor olefins with electron-rich olefins, we have proposed a new initiation mechanism for the spontaneous polymerization observed in many of these systems (Hall 1983). The tetramethylene intermediate, biradical or zwitterionic, was proposed as the common intermediate for both the small molecule reactions and the polymerizations.

As an initiator of cationic polymerization, the tetramethylene intermediate has the disadvantage that the counterion in the propagation reaction is a carbanion. By using electrophilic olefins with a good leaving group in the β-position, non-nucleophilic anions such as the triflate anion can be created as the counterion. Dicyano and tricyanovinyl trifluoromethanesulfonate proved to be very reactive initiators indeed for cationic polymerization (Hall and Rasoul 1984). The following mechanism was proposed for the initiation:



D = donor group, e.g. $-C_6H_4OCH_3$-p

The vinyl trifluoromethanesulfonate initiators were so reactive as to be susceptible to hydrolysis, which made it necessary to prove that the polymerization were not initiated by triflic acid. We now synthesized two less reactive olefins with a leaving group, namely 2,2-dicyanovinyl iodide and 2,2-dicyanovinyl p-toluenesulfonate. Also, polymerizations initiated by the former will be examined for possible living character in view of recent work (Higashimura et al 1983, Higashimura and Sawamoto 1984, Higashimura et al 1984).

Experimental

General: The melting points are uncorrected. The NMR-spectra were recorded on a Varian EM-360 spectrometer. The infrared spectra were obtained on a Perkin Elmer Model 983 spectrophotometer. The elemental analyses were performed by Micanal, Tucson Arizona.

Dichloromethane was purified by consecutive extractions with sulfuric acid, water, aqueous sodium hydroxide, and water, then dried over calcium chloride and distilled from calcium hydride. N-Vinylcarbazole was purified by several recrystallizations from hexane at low temperature, and its purity was checked by HPLC. p-Methoxystyrene and the other monomers were all purified by distillation from calcium hydride. 2,4,6-Tri-t-butylpyridine was obtained from Aldrich and used without further purification.

The molecular weight of the polymers was determined by size exclusion chromatography using Zorbax PSM 60S and 1000S columns in series with chloroform as eluent and a Spectraphysics UV detector at 254 nm. Polystyrene samples were used as standards.

2,2-Dicyanovinyl iodide 1: 2,2-Dicyanovinyl chloride was purified by distillation, b.p. 102°C/30mm Hg. A colorless liquid is obtained which turns red after a few days in the refrigerator at -8°C.

Freshly distilled 2,2-dicyanovinyl chloride (50 mmole, 5.6g) was dissolved in about 50 ml of dry acetonitrile, and 70 mmole (11.6g) potassium iodide was added. The mixture was stirred at room temperature in the dark for 1.5 hours. The salts were filtered off, and the acetonitrile was evaporated without heating. The product was distilled, b.p.73-76°C/0.7mm Hg and crystallized in the receiver. Yield: 5.4g, 50%.

The solid was recrystallized from a minimal amount of ether at -40°C. M.p. 40°C. The crystals are not stable at room temperature.
NMR($CDCl_3$): 9.25 (s) ppm.
IR(KBr): 3080, 3049, 2247, 1541, 1122, 849, 780, 666 cm^{-1}.
Chem. Anal.: Calcd. 23.53%C, 0.50%H, 13.72%N.
Found 23.31%C, 0.39%H, 13.65%N.

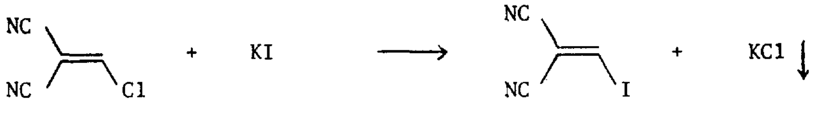
2,2-Dicyanovinyl p-toluenesulfonate 2: Potassium dicyanoethenolate was synthesized by the literature procedure (Josey et al 1967). A solution of the potassium salt was then treated with a warm solution of silver nitrate to produce silver 2,2-dicyanoethenolate.
IR(KBr): 2230, 2177, 1621, 1570, 1394, 1298, 1237, 802 cm^{-1}.

Equimolar amounts of silver 2,2-dicyanoethenolate (4g, 20mmole) and p-toluenesulfonyl bromide (4.7g, 20 mmole) were dissolved in 50 ml of dry acetonitrile and stirred for 5 hours in the dark. The silver bromide was filtered off in a closed system, and the acetonitrile is evaporated at room temperature. The product was purified by two consecutive sublimations at 80°C, and finally by a recrystallization from ether at -40°C, all with a minimal exposure of the product to the atmosphere. The yield is very low (ca 5%).
NMR(CD_3CN): 8.35(s, 1H), 7.8(m, 4H), 2.5(s, 3H)ppm.
IR(KBr): 3069, 2243, 1614, 1593, 1408 cm^{-1}.
2,2-Dicyanovinyl p-toluenesulfonate is stable to water at room temperature.

Polymerization procedure: All the polymerizations were performed under argon atmosphere. The polymers were precipitated in methanol and the yield was determined after drying.

Results and Discussion

Synthesis: 2,2-Dicyanovinyl iodide 1 was synthesized by nucleophilic substitution on dicyanovinyl chloride in acetonitrile at room temperature.



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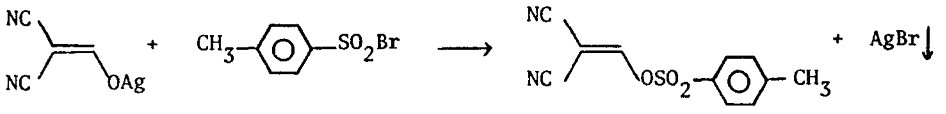
2,2-Dicyanovinyl p-toluenesulfonate 2 was obtained by reacting the silver 2,2-dicyanoethenolate with p-toluenesulfonyl bromide.



2

The reaction is more difficult than those of the trifluoromethanesulfonate initiators described earlier because the p-toluenesulfonyl bromide is less electrophilic than trifluoromethanesulfonic anhydride used earlier.

Polymerization: The first objective of this study was to synthesize other electrophilic olefins with β-leaving groups, in order to demonstrate the generality of our new initiation mechanism. 2,2-Dicyanovinyl iodide 1 can indeed be used as initiator for the cationic polymerization of N-vinylcarbazole and p-methoxystyrene. The other initiator, 2,2-dicyanovinyl p-toluenesulfonate 2, is very difficult to synthesize and was only briefly investigated, but is also very effective. The results of the polymerization experiments are summarized in Table I.

The polymerization of N-vinylcarbazole at low temperature yields polymers with bimodal molecular weights, which could be due to competing free ion and ion-pair propagation. The yields are not quantitative at -45°C, indicating rather slow initiation. This is in contrast to the living polymerization of N-vinylcarbazole initiated by iodine at low temperature[4]. At room temperature low initiator concentrations and low monomer concentrations yield soluble polymer, but in lower yields. High initiator concentration does lead to quantitative yields, but gels are obtained.

The polymerization of p-methoxystyrene initiated by 1 does not go to completion and low molecular weights are obtained.

The initiating ability of 2,2-dicyanovinyl p-toluenesulfonate 2 was only investigated with p-methoxystyrene. Moderate yields and molecular weights are obtained.

As expected, these two initiators were much less reactive than 2,2-dicyanovinyl trifluoromethanesulfonate and tricyanovinyl trifluoromethanesulfonate described in a previous communication[2].

The polymerization of N-vinylcarbazole initiated by 1 was also investigated in the presence of a radical inhibitor, bis-(3-t-butyl-4-hydroxy-5-methylphenyl)sulfide. The polymerization proceeded unchanged proving that no radicals are involved.

Table I: Polymerization Results.

Monomer (mole/l)		Initiator (mole %)		Temp °C	Additives	Yield (%)	Molecular Weight
NVCZ	1.0	1	1.0	-45	-	97**	300,000 45,000
	1.0		1.0	-45	c)	95**	500,000 80,000
	1.0		1.0	-45	b)	86	17,000
	0.2		1.0	-45	-	87	40,000
	0.2		0.3	-45	-	58	40,000
	1.0		0.1	27	-	96	50,000
	1.0		1.0	27	-	100	*
	1.0		1.0	27	a)	93	10,000
	1.0		1.0	27	b)	89	6,000
	1.0		1.0	27	a)+b)	94	10,000
	0.2		1.0	27	-	88	30,000
	0.2		1.0	27	a)	83	2,000
	0.2		1.0	27	b)	79	2,000
PMS	1.0	1	1.0	27	-	81	5,000
	1.0		1.0	27	a)	0	
	1.0		1.0	27	b)	0	
	1.0		0.5	27	-	76	5,000
	1.0		0.5	27	b)	0	
	1.0	2	0.8	27	-	82	12,000
	1.0		1.2	27	-	82	8,000
	1.0		1.2	27	a)	0	

Polymerization conditions: in sealed tubes under argon atmosphere in dichloromethane for 16 hours at 28 C.

NVCZ = N-vinylcarbazole, PMS = p-methoxystyrene

a) 2,4,6-tri-t-butylpyridine 2 mole %

b) tetrabutylammonium iodide 0.5 mole %

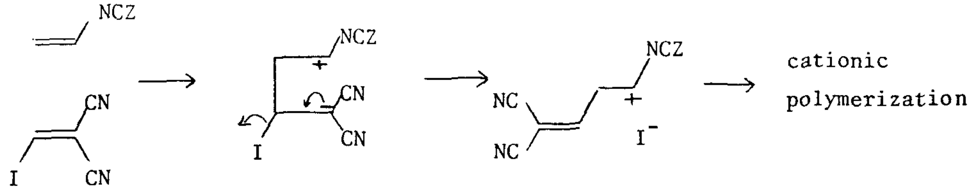
c) bis-(3-t-butyl-4-hydroxy-5-methylphenyl)sulfide

* cross-linked polymer (gel)

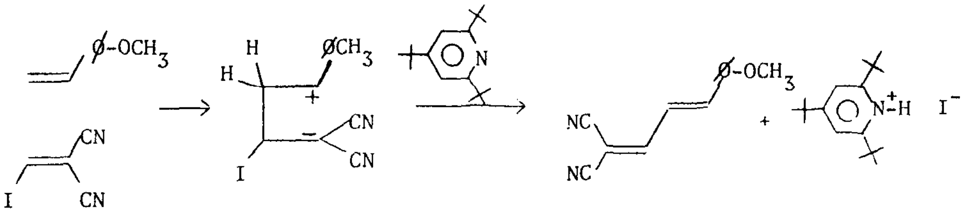
** bimodal polymer

No proton initiation: Initiation by a proton acid formed by adventitious hydrolysis of the two olefins **1** and **2** can be ruled out. 2,2-Dicyanovinyl iodide **1** is stable for several hours at room temperature, and 2,2-dicyanovinyl p-toluenesulfonate **2** is stable in water for several hours, which is in sharp contrast to the electrophilic vinyl trifluoromethanesulfonates studied earlier.

In the case of N-vinylcarbazole, the polymerization proceeds in the presence of a proton trap. 2,6-Di-t-butylpyridine and 2,6-di-t-butyl-4-methylpyridine have been used by other investigators to distinguish between different initiation mechanisms (Kennedy and Chou 1982, Moulis et al 1980): polymerization will not proceed if the initiation involves proton transfer. We used 2,4,6-tri-t-butylpyridine, because 2,6-di-t-butylpyridine forms charge-transfer complexes with our electrophilic olefins; the trisubstituted derivative does not, due to increased steric hindrance around the ring. The fact that the polymerization of N-vinylcarbazole initiated by 2,2-dicyanovinyl iodide **1** proceeds in the presence of this proton trap, proves that the initiation does not involve proton transfer. The tetramethylene intermediate is formed and after elimination of the leaving group, the carbenium ion initiates the polymerization.



In the case of p-methoxystyrene, the polymerization is inhibited by the addition of 2,4,6-tri-t-butylpyridine. We can postulate that in this case the proton trap is able to abstract the proton of either the tetramethylene or of the propagating carbenium ion, due to its higher acidity and less steric hindrance compared with the case of N-vinylcarbazole.



In the polymerization of isobutylene, Kennedy and his coworkers describe a similar case in which 2,6-di-t-butylpyridine is able to terminate the polymerization by abstraction of a non-hindered methyl proton from the propagating carbenium ion (Kennedy and Chou 1982).

Is the iodide polymerization living?: Recently, several papers have been published on living cationic polymerizations (Higashimura and Sawamoto 1984). Propagating carbenium ions of donor olefins have been shown to be stable when the gegenion is I_3^-. In the case of N-vinylcarbazole a living polymerization can be obtained in dichloromethane at -78°C, using iodine as initiator.

The possible living character of our system was more closely investigated. At low temperature, bimodal molecular weights are observed, and the yields are low. At room temperature the molecular weights do not correspond to the theoretical molecular weights, and also the yields are not quantitative at lower monomer concentrations. The addition of a common ion source, tetrabutylammonium iodide, to reduce the dissociation of the growing center only results in even lower molecular weights. Non-polar solvents, which are known to encourage living character, cannot be used due to the insolubility of the monomer and polymer.

We can conclude that the polymerizations using **1** as initiator and involving I^- as the gegenion are not living, confirming the work of Higashimura and Sawamoto.

Conclusions: Two new initiators are described lending more evidence to the tetramethylene theory. 2,4,6-tri-t-butylpyridine does not inhibit the initiation of N-vinylcarbazole by 2,2-dicyanovinyl iodide, proving that no proton transfer is involved in the initiation step, and thus proving the existence of a tetramethylene intermediate. After elimination of the leaving group, the carbenium ion initiates the polymerization and the leaving group acts as counterion. No living character was observed in these polymerizations. The ability of the water-stable 2,2-dicyanovinyl p-toluenesulfonate to initiate cationic polymerization proves that adventitious acid is not responsible for these polymerizations.

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