Polymer Bulletin 27, 17–24 (1991)

Polymer Bulletin

Cationic polyelectrolytes

IX. New aspects of poly(*N,N*-dialkylaminoalkylacrylamides) synthesis via nitrile group reaction of polyacrylonitrile with *N,N*-dialkylaminoalkylamines

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Synopsis

The aminolysis-hydrolysis of the nitrile groups of PAN with asymmetrical diamines as $H_2N-(CH_2)_m-NR_2$ was investigated by IR spectroscopy (qualitative and quantitative) and elemental analyses. IR quantitative spectroscopy is an adequately proved method for investigation of the extent of transformation. The amine reactivity depends on the distance between the two amine groups and the size of the alkyl substituents on the tertiary amine. The data support the reaction mechanism by the nucleophilic attack of the primary amine on the two neighbouring nitrile groups.

Introduction

The synthesis of cationic polymers of poly(N,N-dialkylaminoalkylacrylamide) via the reaction of the nitrile-groups of macromolecular compounds with N,N-dialkylaminoalkylamines in the presence of water was previously demonstrated (1,2). Hence this method was applied to the synthesis of polymers analogus to bloc (3) and graft copolymers (4) of N,N-dimethylaminopropylacrylamide with acrylic acid.

This paper attempts to supply additional information concerning the amynolysis-hydrolysis reaction mechanism of nitrile groups from PAN with asymmetrical diamines of $H_2N-(CH_2)_m-NR_2$ type, where m = 2,3,4 and R is $-CH_3$, $-C_2H_5$, $-C_4H_9$, $-CH_2-CH_2-OH$. Some of previously followed reactions (1) were repeated at lower temperatures. The degree of conversion was determined by IR-spectral analysis (qualitative and quantitative transformations).

Experimental

Materials

Acrylonitrile (practical grade) was dried on $CaCl_2$ and distilled at 760 mm Hg; the 76-77°C fraction was used.

Polyacrylonitrile (PAN) was synthesized and purified as previously reported (1). A polymer with $\overline{M}_v$ = 110,000 was used. Asymmetrical diamines, N,N-dimethyl-1,2-diaminoethane (DMDAE)

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N,N-diethyl-1,2-diaminoethane (DEDAE), N,N-dimethyl-1,3-diamino-propane (DMDAP), N,N-diethyl-1,3-diaminopropane (DEDAP), N,N-dibuthyl-1,3-diaminopropane (DBDAP), N,N-diethyl-1,4-diaminobutane (DEDAB), supplied by BASF Co., were distilled at low pressure before use. N,N-Bis(2-hydroxyethyl)-1,3-diaminopropane (DHEDAP), and dimethylsulfoxide (DMSO) were analytical grade and were used without further purification.

Methods

The reactions of PAN with N,N-dialkylaminoalkylamines were carried-out in the presence of water in a three necks flask fitted with a stirrer, thermometer and reflux condenser. The reaction parameters are shown in Table 1.

Table 1. Conditions of Reaction between PAN-N,N-Dialkylamino-alkylamines

Exp.	Amine	Temp. (°C)	Time (h)	Molar ratio	
				Amine/CN	H_2O/CN
1	DMDAE	105	22	6/1	4/1
2	DEDAE	110	14	5/1	4/1
3	DMDAP	115	12	5/1	-
4	DMDAP	110	10	5/1	1/1
5	DMDAP	110	10	5/1	4/1
6	DEDAP	110	12	5/1	4/1
7	DBDAP	110	18	4/1	4/1
8	DHEDAP	110	12	4/1	2/1
9	DEDAB	110	10	5/1	4/1

Recovery of the reacted polymers was carried-out by dissolving them in methanol, after first removing the excess amine and water by vacuum evaporation. This was followed by precipitation of the polyelectrolyte products in anhydrous diethyl ether at 0°C. This technique was used for the polymers reacted with DMDAE, DEDAE, DMDAP, DEDAP and DBDAP. The polymers reacted with DEDAB and DHEDAP were precipitated into acetone. After isolation, the polymers were redissolved in methanol and reprecipitated as above.

IR-Spectroscopic Analyses

IR spectra were recorded on a Perkin-Elmer 577 IR spectrophotometer within the range of 4000-400 cm^{-1} using KRS-5 (thalium bromide and iodide) crystals as supports. In order to quantitatively determine the transformation degree of the nitrile groups to substituted amide groups as a function of the reaction time, a calibration curve was first plotted. For this reason, the mixtures of PAN and polyelectrolyte A_3 (PAN completely reacted with DMDAP) were prepared. The concentration of these mixtures was known exactly. Solutions of $\simeq$ 5 % (wt) concentration of these mixtures in DMSO were caste on the KRS-5 crystals yielding films with approximately equal thicknesses. The 2240 cm^{-1} ($-C\equiv N$) and 1650 cm^{-1} (amide groups) were chosen for analysis. From the IR-spectra of the PAN and polyelectrolyte A_3 mixtures, the absorbancy (A) of these bands was determined applying the base line method (5). The A_{1650}/A_{2240} ratio (R) plotted against the concentration of the two polymers gives the calibration curve (Fig. 1).

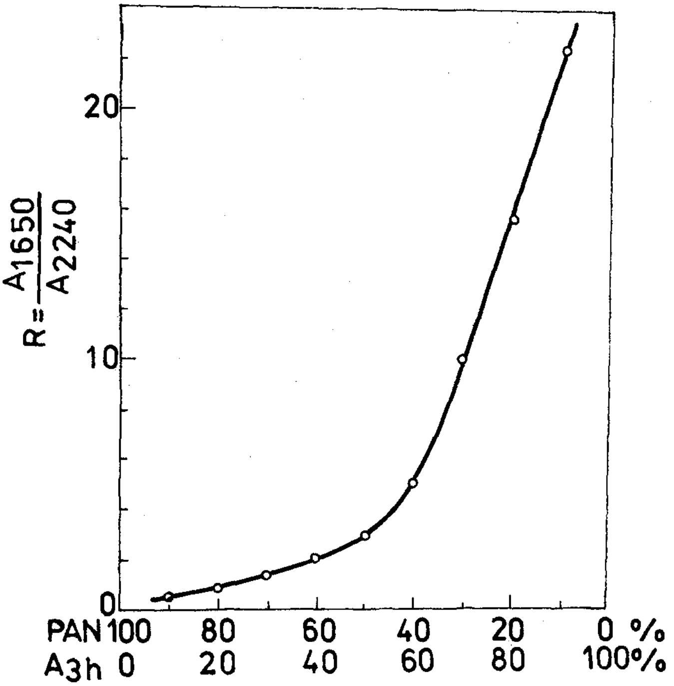


Figure 1: The calibration curve used to follow the transformation degree of CN groups from PAN in the substituted amide groups, applying ir spectral analysis method.

The polymers isolated from the reaction mixtures were also dissolved in DMSO and caste as films on the KRS-5 crystals. The ratio (R) was determined from the IR-spectra of the samples at different reaction times. The amide content of the polymers was determined from the calibration curve.

RESULTS AND DISCUSSION

The reaction of the nitrile groups of PAN with asymmetrical diamines in the presence of water was chosen as a way to synthesize cationic polyelectrolytes with tertiary amine groups for the following reasons:

- the nitrile groups of PAN readily form six member rings with the primary amines via an initial imidine ring (6,7);
- the glutaronitrile (GN) reaction with primary aliphatic amines in the presence of water without a catalyst leads to glutaramide disubstituted with amine radical (8).

When the reaction of GN with DMDAP was performed in the presence of water for 50 hrs, N,N'-bis(3-dimethylaminopropyl) glutaramide is obtained (1). The formation of this compound might be rationalysed by assuming that in the first reaction stage the primary amine group and the two nitrile groups are in a position which favours formation of an imidinic ring. Alkaline hydrolysis of this compound would lead to the substituted glutarimide which in the presence of excess asymmetrical diamine is converted into the disubstituted glutaramide.

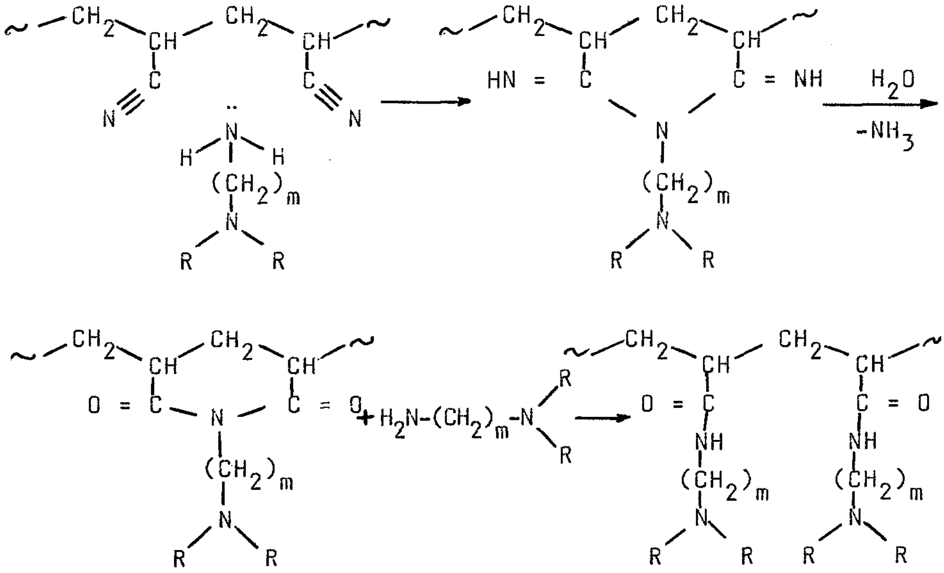
The reactions of PAN with DMDAP were first performed without water. After a reaction of 12 hrs (Table 1, exp. 3) PAN changed from a white powder into a dark red material which was insoluble in any solvent. The IR spectrum of this product contains absorption bands at 1660 cm^{-1} and 1590 cm^{-1} assigned to -C=N- bond which reinforces the hypothesis that the insoluble properties of polymer are due to cyclization reactions. The reaction of PAN with DMDAP in the presence of water leads to soluble polymers (Table 1). The color of the polymer is influenced by the H_2O/CN molar ratio as follows: dark orange for the molar ratio of 1 mol H_2O/1 mol CN and light yellou for the molar ratio of 4 moles H_2O/1 mol CN. Consequently, the reaction of the nitrile group of PAN with ω-N,N-dialkylaminoalkylamines requires the latter condition.

The first evidence for the chemical transformation of PAN with asymmetrical diamines in the presence of water are provided by IR-spectra, which show the disappearance of the nitrile band (2240 cm^{-1}) and appearance of the characteristic bands for substituted amide groups as follows:

- a strong band at 1650 cm^{-1} determined by the stretch vibrations of C=O bond (amide band I);
- a band of medium intensity at 1540 cm^{-1} assigned to the deformation vibration of NH bond (amide band II);
- an absorption band from 1260-1280 cm^{-1} assigned to the stretch vibrations of C-N bonds contained by O=C-N groups.

The aminolysis-hydrolysis reaction of the nitrile groups of linear polymers with asymmetrical diamines in the presence of water can be emphasized by means of Scheme I.

Scheme I



The proposed structures for poly(ω-N,N-dialkylaminoalkylacrylamides) which might be performed accordingly to Scheme I are listed in Table 2.

Table 2. Expected Structures for Poly(ω-N,N-dialkylaminoalkylacrylamides)

Amine	m	R	Cationic Polyelectrolyte (from scheme I)
DMDAE	2	CH_3	A_1
DEDAE	2	C_2H_5	A_2
DMDAP	3	CH_3	A_3
DEDAP	3	C_2H_5	A_4
DBDAP	3	$n\text{-}C_4H_9$	A_5
DHEDAP	3	CH_2CH_2OH	A_6
DEDAB	4	C_2H_5	A_7

The imidinic ring formation during the first stage of the process is possible as a consequence of the nucleophilic attack of the primary amine on the two neighbouring nitrile groups. This intermediate compound determined PAN cyclization in the absence of water and the reaction of GN, with primary aliphatic amines, respectively. The chain cyclization reaction via proton migration from $C\alpha$ can be avoided by the hydrolysis reaction of imidine ring towards imide. It could be also assert that imidine performed during the first reaction stage would be hydrolysed to imides because amidine compounds are easily hydrolysable to amide compounds just heating in weak alkaline aqueous solutions (9).

The fact that the color of the yielded polymer depends on the H_2O/CN molar ratio is a proof that a faster hydrolysis of imidine breakes the proton migration from tertiary carbon atom, which also determined the permanent coloring of thermal treated PAN (10,11). The substituted acrylamide units result, probably, via amynolyse reaction of the imide. Disubstituted succinamides result by the aminolyse reaction of succinimide with primary aliphatic amines of medium basicity (12).

The nucleophilic attack of primary amines on the nitrile groups is also grounded by the fact that amine reactivity depends on its chemical structure. The total reaction time (up to - C≡N band disappearance) depends on the substituents of tertiary amine group and the distance between the two amine groups. For the same temperature and molar ratio (for N,N-dialkyl-1,3-diaminopropan, Table 1) the following reactivity series was noticed: DBDAP < DEDAP < DMDAP. The reaction time up to the 2240 cm^{-1} band disappearance was 18, 12 and 10 hrs, respectively. The upper nucleophilic of DMDAP is determined by a larger accesibility of the primary amine group when both substituents of nitrogen are $-CH_3$.

Nucleophilic reactivity of the asymmetrical diamines increases in these reactions at the same time with the distance between primary and tertiary amine groups. The remark was proved by the following reactivity series: DEDAE < DEDAP < DEDAB the reaction time being 14, 12 and 10 hrs, respectively, for the same temperature and molar ratios (Table 1).

The elemental analysis data of poly(ω-N,N-dialkylamino-alkylacrylamides) (the maximum extent of transformation) are listed on Table 3.

Table 3. Elementary Analysis Data for Poly(ω-N,N-dialkylamino-alkylacrylamides)

Cationic polymer of Tab.2	Theoretical structure unit formula	Elementary analysis (%)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
A_1	$C_7H_{14}ON_2$	59.15	59.07	9.86	10.25	19.72	20.03
A_2	$C_9H_{18}ON_2$	63.53	62.93	10.59	10.38	16.47	16.65
A_3	$C_8H_{16}ON_2$	61.54	61.65	10.25	10.51	17.95	17.62
A_4	$C_{10}H_{20}ON_2$	65.22	64.89	10.87	10.62	15.21	15.45
A_5	$C_{14}H_{28}ON_2$	70.00	68.95	11.66	11.52	11.66	12.05
A_6	$C_{10}H_{20}O_3N_2$	55.55	55.88	9.26	9.07	12.96	13.45
A_7	$C_{11}H_{22}ON_2$	66.66	65.73	11.11	11.13	14.14	14.50

Table 3 shows that experimental data and those calculated for the structural unit of ω-N,N-dialkylaminoalkylacrylamide (Scheme I) are in good agreement. The data support the mechanism in Scheme I.

Quantitative Determination of the Nitrile Group Transformation

The nitrile group transformation into N,N-dimethylamino-propylacrylamide during the PAN reaction with DMDAP was investigated by means of IR-spectroscopy. The R ratio was calculated from IR-spectra for the corresponding samples of different reaction times. The amide content was determined by means of the R value and the calibration curve (Fig. 1). Figure 2 gives the values as function of the reaction time. The nitrile group transformation into amide ones during the PAN reaction with DMDAP is almost total after 9 hrs.

The IR-analysis of the polymer samples after the first hours of the reaction shows, besides the band characteristic to $-C\equiv N$ (nonreacted) and substituted amide groups, a weaker intensity band at 1590 cm^{-1} (Fig. 3). The band at 1590 cm^{-1} shows

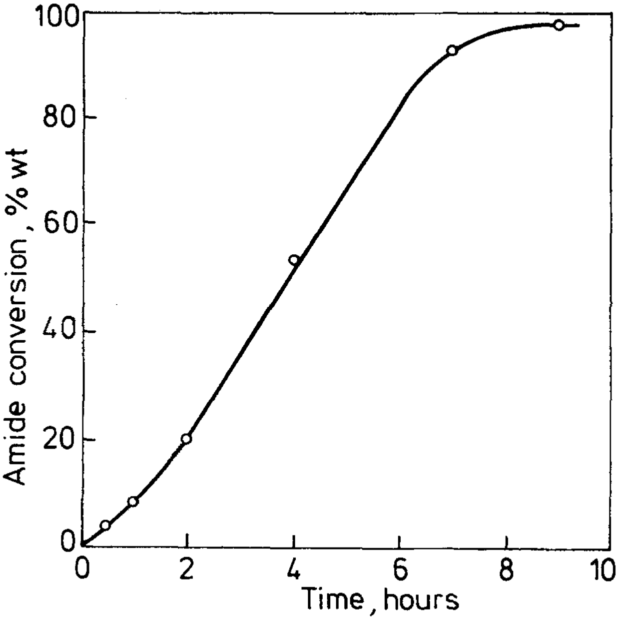


Figure 2 : Variation of transformation degree of nitrile groups into amide ones during the reaction of PAN with DMDAP.

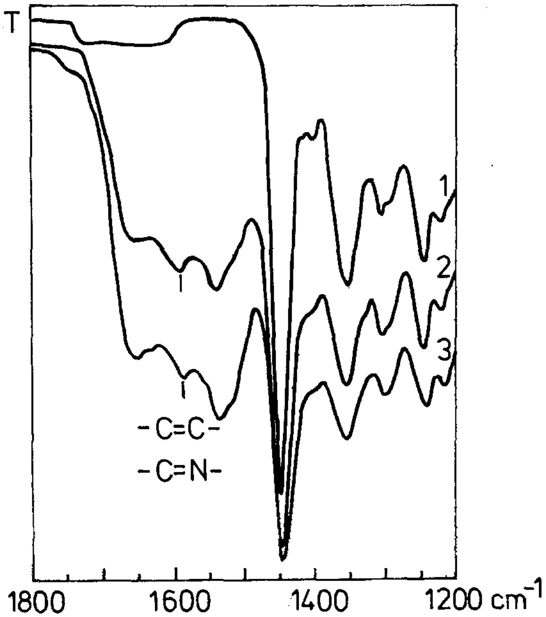


Figure 3 : IR spectra of the yielded polymers from the reaction of PAN with DMDAP comparatively with PAN; (1) - PAN; (2) - after 30 min. of reaction; (3) - after 60 min. of reaction.

the existence of the - C = N - groups characteristic to the intermediate imidinic compound according to the Scheme I.

The presence of this band together with those characteristic to amide group shows in the one hand the existence of imidinic ring in an intermediary transformation stage and on the other hand the instability of such bonds towards the hydrolyse reaction.

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Accepted July 23, 1991 C