Anionic Polymerization of Acrylonitrile with Trivalent Phosphorus Compounds

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In order to see if the anionic polymerization of acrylonitrile initiated by trivalent phosphorous compounds is a living polymerization, and to see how high the molecular weight of polyacrylonitrile can be reached, the polymerization of acrylonitrile using triethylphosphite (TEP), phenyldiethoxyphosphine (PEP) and diphenylethoxyphosphine (DPP) was investigated. TEP was found to be a better initiator than the others, producing polymers with extremely high molecular weights. The polymerization system is a living type as the molecular weight increases until the system is exposed to air. However, the molecular weight polydispersity was in the range of 2.2–2.6 due to the complexity of initiation. The average molecular weight (Mw) reached 375,000, while that of a commercial polyacrilonitrile obtained by emulsion polymerization was 113,000. The polymer solutions obtained by the anionic polymerization became gel on standing, but they became sol when more solvent (DFM) was added and heated. The majority of polymers were slightly yellow due to the formation of imide linkages. The copolymerization with methylacrylate resulted in low molecular weight copolymers, with a ratio of acrylonitrile to methylacrylate units of 10.

Keywords   acrylonitrile, anionic polymerization, phosphite initiation

Introduction

The anionic polymerization of acrylonitrile (AN) using metal initiators such as dimethyl-aminotitanium compounds (1), and butyl lithium (2), has been studied some decades ago, and it has been concluded that polyacrylonitrile (PAN) with high molecular weight cannot be obtained because of various side reactions such as chain transfer reactions, strong interaction between metal cations with propagating PAN anion, and the conversion of propagating carbanion ($-CH_2-CH^- -C\equiv N$) to inactive imino anion ($-CH_2-CH=CN^-$). Raynal has studied the anionic polymerization of AN and methacrylonitrile using initiators consisting of sodium amide and alkoxides, and obtained PAN with molecular weights of only several thousands (3). More recently, nitrogen anion tetraalquilammonium salts, such as tetrabutylammonium-carbazolide, is said to be a useful anionic initiator for polar vinyl monomers, including acrylonitrile (4), and a bright yellow PAN has been obtained.

L. Jiang and coworkers have reported anionic polymerization of AN initiated by samarium diidodide (5). They have obtained PAN with Mw up to 35,000, and proposed a mechanism of formation of AN radical anion, which combine to give dianion for propagation. It is known that phosphine and ammonia undergo the cyanoethylation with AN (6, 7). The trivalent phosphorus compounds are soft bases, and add to the double bonds of AN (soft acid) without abstraction of the monomer proton. The polymerization of AN using triphenylphosphine has been reported, but obtained PAN had low molecular weight (8). A Zwitterion mechanism has been suggested for the polymerization. It has also been suggested that at a higher temperature such as above 50°C, the Zwitterion abstracts proton from AN to give a monomer anion which initiates the polymerization (8). The present author previously reported the polymerization of AN using triethylphosphite (TEP) (9), and showed that high molecular weight PAN could be obtained by the polymerization at room temperature in dimethylformamide (DMF) (10). The 30% concentration of PAN in DMF ready for spinning fibers can easily be obtained by this polymerization. The addition of tetraethylammonium bromide somewhat increased the rate of polymerization probably due to the exchange of the phosphonium counter cation with the ammonium cation, which will not interact strongly with the propagating carbanion as nitrogen does not possess *d*-orbitals to accommodate the carbanion (10). Anionic polymerization of AN by Cy_3PCuMe has been reported recently (11), in which the phosphine, Cy_3P, adds to AN similarly to the above studies.

There is a limit in molecular weight in the free radical initiated suspension or emulsion polymerization of AN, because the polymerization is heterogeneous due to the insolubility of PAN in its monomer. The use of solvents, which dissolve polyAN, in free radical polymerization decreases the molecular weight and rate of polymerization due to the interaction of electron deficient PAN radicals and basic solvents such as DMF, especially when DMF contains impurities such as dimethylamine.

PAN is one of the starting materials for manufacturing carbon fibers, and it is of interest to obtain extremely strong carbon fibers if very high molecular weight PAN is used. In this work therefore, in order to see how high the molecular weight of PAN by anionic polymerization can be reached, the polymerization of AN in dimethylformamide (DMF) was reinvestigated using a three trivalent phosphorus compounds; triethyl-phosphite (TEP), phenyldiethoxyphosphine (PEP), and diphenylethoxyphosphine (DPP). The anionic copolymerization with an acrylate was also attempted.

Experimental

Materials

AN used was an industrial product donated by Celulosa y Derivados, SA, and it was distilled repeatedly over calcium hydride under dry nitrogen. TEP was supplied by Fluka and it was also distilled over calcium hydride before use. DMF was also given by the company and it was distilled repeatedly over calcium hydride. Tetrabutylammonium bromide (Aldrich) was dried at 100°C in vacuum before use. DPP was synthesized by the reaction of diphenylchlorophosphine (Aldrich) with ethanol. A solution of 46.4 g (36 mL, 0.2 mol) of the freshly distilled phosphine in 20 mL of dry n-hexane, was added slowly with stirring at 0°C to a mixture of 11.6 mL of dry ethanol, 16 mL of dry pyridine and 200 mL of n-hexane. The system was allowed to reach room temperature, and pyridine hydrochloride was filtered off and the solvent was evaporated under a reduced pressure. The remaining product was distilled in vacuum and a fraction boiling at

162–166°C/28 mmHg was collected. The second distillation yielded 20.3 g of PEP. ^{31}P NMR: 111 ppm (in C_6D_6). PEP was synthesized similarly to DPP. A solution of 27 mL of phenyldichlorophosphine (Aldrich) (35.8 g, 0.2 mol) in 20 mL of n-hexane was added slowly to a mixture of 23.2 mL of dry ethanol, 32 mL of dry pyridine and 200 mL of n-hexane at 0°C. After stirring for an hour, the salt was filtered off, and the solvent was distilled off under a reduced pressure. The residue was distilled twice under a reduced pressure and 13.9 g of PEP biling at 78–81°C/28 mmHg were obtained. ^{31}P NMR: 155 ppm (in C_6D_6).

Polymerization

The polymerization was carried out at room temperature (≈20°C) in a 50 mL two-necked flask under argon flow, which was passed through a tube packed with calcium hydride powder. The system was stirred with a magnetic stirrer. The polymer was precipitated in methanol, filtered, washed with methanol and dried in a vacuum desiccator. The yields were calculated from the weights of polymers. This method is not as strict as that for the living anionic polymerization of hydrocarbon monomers, and therefore, the results depended significantly on the atmospheric humidity. A larger scale polymerization was carried out using a 500 mL two-necked flask. The polymerization system was dried under vacuum using a heat gun to remove moisture on the surface of flask, and the reactants were added under argon gas dried by passing a column of calcium hydride.

Molecular Weight Determination

GPC using DMF as asolvent gave an abnormally high molecular weight due to the dipole-dipole interaction between polymer chains, and therefore, intrinsic viscosity was determined, and the number and weight average molecular weights were calculated from the following equations, respectively. The polydispersity was calculated from the ratios of Mn and Mw.

$$[\eta] \text{ (g/100 mL)} = 39.2 \times 10^{-5} \text{ Mn}^{0.75} \tag{12}$$

$$[\eta] = 6.98 \times 10^{-4} \text{ Mw}^{0.65} \tag{13}$$

Results and Discussion

Table 1 shows some of the typical results of polymerization. The molecular weight (MW) reached more than three times greater than that of a commercial PAN commercially prepared by emulsion polymerization. The increase in MW with polymerization time indicates that the polymerization is a living anion polymerization. However, the Mn calculated from the molar ratio of the monomer and the initiator, assuming that each initiator initiates the polymerization, is much less than the Mn of polymers obtained. This indicates that not all but a minor fraction of TEP is taking part for the initiation, and suggests that the rate of initiation is much slower than that of propagation. Even after the polymerization ended, the system smells strongly of TEP, also indicating that only a certain portion of TEP was used for initiation. When equimolar amounts of TEP with AN were mixed at room temperature, the system became hot and within a few minutes, the system solidified consuming all AN, and yellow PAN was obtained (Scheme 1). The molecular weight determined from intrinsic viscosity in DMF was found to be 3300 (Mn) and 4700

Table 1
Polymerization of AN initiated by with triethylphosphite (TEP)

| Run	[P(OEt)$_3$] (mol/L)	[AN]/[P(OEt)$_3$]	Calculated Mn^a × 10^{-3}	[NBu$_4$Br] (mol/L)	Polymerization time (h)	Yield (%)	Mw × 10^{-3}	Mn × 10^{-3}
3A	0.012	434	23.03	0.041	2	89	203	86
4	0.008	651	34.6	0.041	2	86	164	71
5A	0.004	1302	69.1	0.041	2	74	227	94.5
34-1	0.008	651	34.56	0.031	0.5	38	135.3	60.4
34-2	”	”	”	”	0.8	64	154	67.5
34-3	”	”	”	”	1.2	76	160	70.0
34-4	”	”	”	”	1.5	82	171	74.2
34-5	”	”	”	”	2.2	85.6	178	76.5
34-6	”	”	”	”	4	92	180	77.3
36	0.008	651	34.56	0.011	2	—	205	86.6
37-1	”	”	”	0.015	1	55	328	130
37-2	”	”	”	”	2	75	360	141.2
37-3	”	”	”	”	3	84	375	146
39-1	”	”	”	”	1	67	270	110
39-2	”	”	”	”	2	75	290	117
39-3	”	”	”	”	3	86	298	120
39-4	”	”	”	”	4	87	306	122
Com-PAN							113	52

^{a}Assumed that each phosphite initiated polymerization 53 × [AN]/[P(OEt)3].

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(Mw). Assuming that each polymer chain contained one TEP unit, and that no chain transfer occurred, only 0.016 mol out of 1 mol of TEP was found to be used for initiation. From the elemental analysis (C: 66.09; H: 5.41; N: 25.43; and P: 0.60%) of the product, calculation of the degree of polymerization assuming the structure: $(EtO)_2P(O)-(CH_2-CHCN)_n$ resulted in n = 52 (Mn = 2770) from C% and n = 53 (Mn = 2800) from N%, but from the n from P% was found to be 95 (Mn = 5035). The deviation of Mn from P content from those from C and N contents is due to analytical error due to its small amount. It can be seen that a small fraction of TEP is used for initiation (Scheme 2).

When the reaction was carried out by adding AN (4 mL) dropwise over a period of 80 min to a mixture of TEP (10 mL) and toluene (20 mL), 2.5 g (78% yield) of a pale yellow solid precipitated. The Mn and Mw of the product were found to be 870 (DP = 14) and 1020, respectively. Elemental analysis of the product (C: 64.94; H: 5.57; N: 23.94; and P: 1.24%) gave calculated degrees of polymerization; n = 31 (Mn = 1643) from C, 20 (Mn = 1075) from N and 45 (Mn = 2390) from P. In this case, it also seems that less than a half of the polymer chains contained the TEP fragment. These results show that only a fraction of TEP participates in initiation, and chain transfer reactions inevitably take place.

When equimolar amounts of TEP with AN were mixed at room temperature in the presence of an excess amount of water, an exothermic reaction took place. After being left to stand for a few days, the characteristic odor of TEP disappeared, and ethanol was liberated. Water was distilled off, and the remaining liquid products were distilled at $48°C/0.25$ mmHg and $110-114°C/165$ mmHg (main product), were obtained. In this case, no solid product was formed, which indicates the Zwitterion is quickly destroyed by water. ^{1}HNMR spectra of the main product are shown in Figure 1. The peaks correspond to the product of the addition of TEP to AN (Scheme 3). The NMR spectra of the minor product consisted principally of the peaks of ethyl groups and very small amounts of peaks due to impurities, and obviously does not contain AN, but it no longer had the characteristic odor of TEP. It seems that TEP reacts with water when heated. The addition reaction was exothermic and TEP reacted with water to give a pentavalent phosphorus compound. From these observations, it is thought that the addition of TEP to AN is relatively fast, but the addition of monomeric and dimeric Zwitterions to monomer is rather slow, and once trimeric Zwitterion is formed, the propagation proceeds very rapidly (Scheme 4). Products of Arbusov type reaction and a cyclic phosphorane, from the Zwitterions, may be formed, but an attempt to isolate these products from the polymerization systems was not successful.
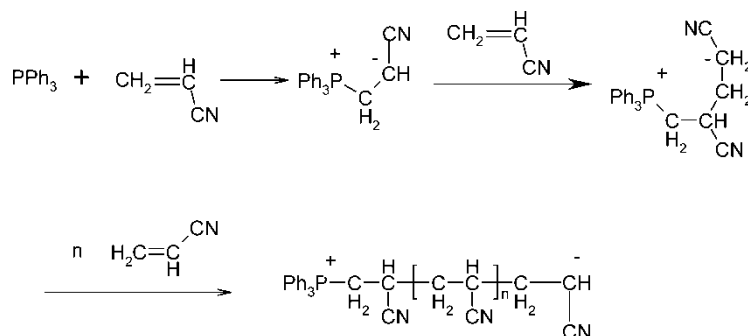
**Scheme 1.** Polymerization of AN initiated with triphenylphosphine.
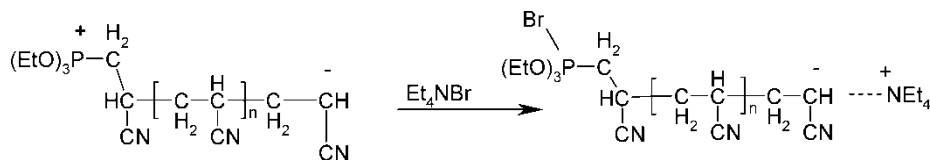
Scheme 2. Change in the counter cation.

The molecular weight tends to increase with a decrease in the initiator concentration as expected. The concentration of tetrabutylammonium bromide does not seem to influence the polymerization within the range of concentrations of this work. Also, in the previous study (10), the presence of tetraethylammonium bromide did not influence the molecular weight much, although the rate of polymerization was increased significantly by the presence of ammonium salt. The polydispersity from the ratios of Mw to Mn was found to be 2.2–2.6, which is very large for living anionic polymerization, and is the same as that of free radical polymerization. This is, again, due to the slow initiation process due to the formation of less reactive monomer and dimer Zwitterions. In Table 1, the molecular weights differ somewhat depending on the experiments, and this is because of the traces of moisture in the polymerization system. In order to obtain extremely high molecular weight PAN, a completely dry system should be employed. Since it is impossible for the polymerization system of this work to eliminate moisture completely, the molecular weight depends on the moisture in the system. It is worth mentioning that the polymerization could be carried out only during the dry season (December to April in Mexico City).

Table 2 shows the results on the effect of the additional monomer. It can be clearly seen that MW increases by the further addition of monomer, indicating that the propagating anion was alive and continued to propagate when more monomer molecules enter the system. It is noteworthy that the polydispersity does not change appreciably by the further addition of monomer.

Tables 3 and 4 show the results of polymerization using the two phenyl phosphines, PEP and DPP, as initiators. The molecular weights were lower than the cases of TEP, and especially DPP having two phenyl groups was poorer initiators, indicating that the phenyl group has a negative effect for the polymerization. Triphenyl phosphine (TPP) did not give a polymer under the same conditions in this work. However, when the polymerization system is heated to around 50°C or higher, low molecular weight yellow to orange
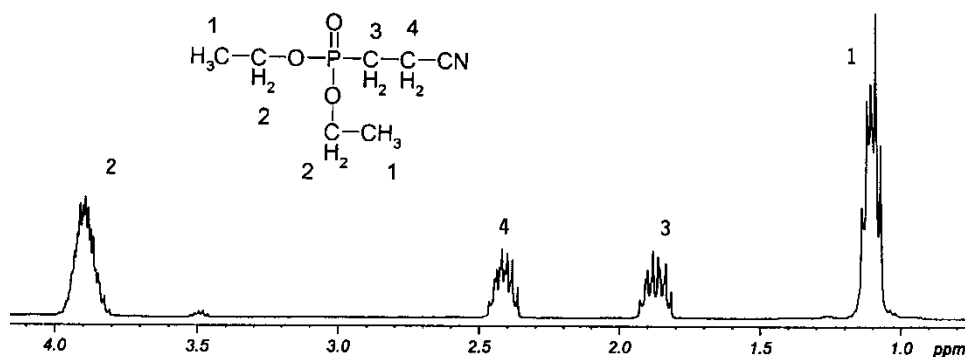
Figure 1. ^{1}H NMR spectrum of the adduct of TEP and AN (in CDCl$_3$).
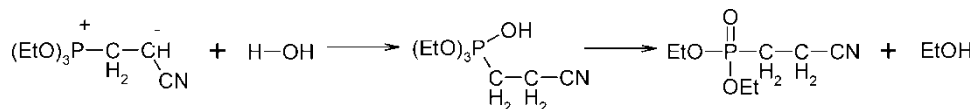
Scheme 3. Reaction of monomeric Zwitterion with water.

colored polymer was obtained. The reason why the phenyl group on the trivalent phosphorus compounds acts negatively for the anionic polymerization of AN, is probably because the phenyl group will decrease the basicity of the phophine and increases the softness. In the case of these phenylphosphines, the observed Mw are much higher than the Mn calculated from the ratio of AN and phosphines, suggesting that the monomeric and dimeric Zwitterions are rather stable and a fraction of them participate in propagation. It seems that the interaction between the propagating AN carbanion and the phosphonium cations increases by the introduction of the phenyl group. The triethoxyphosphonium cation should have a lower positive nature because of the surrounding three electron donating ethoxy groups. But, in the cases of phenylphosphonium cations, the positivity increases, increasing the interaction with the propagating carbanion. There seems to be no significant effect of the ammonium salt on the polymerization.

Figure 2 shows IR spectra of PAN initiated by DPP (sample 14). The absorption at $1667 \, cm^{-1}$ is due to the imide linkages and that at $1599 \, cm^{-1}$ is due to the phenyl group of DPP. The polymer with PEP also showed an identical spectrum to this. Naturally, the polymers obtained with TEP and with AIBN in toluene did not have these peaks. When the polymerization temperature is raised, the peak due to the imide linkages, appear even with TEP initiation. The propagating anion attacks the carbon atom of nitrile group and the imino anion continues to attack the carbon of the adjacent nitrile group. Since the obtained polymers are yellow in color, conjugated cyclic imide likages are thought to be formed.

Table 5 shows the results of copolymerization with methylacrylate (MA). The rate is slowed down significantly by the presence of MA. When the concentration of MA is increased, small amounts of sticky polymers were obtained. Copolymer 2 has a higher molecular weight than copolymer 1, although the concentration of MA is higher. This is because copolymer 1 was prepared under a condition stricter to moisture. TEP did not polymerize methacrylonitrie methylacrylate, but can add to methylvinylketone at room temperature, giving only a viscous liquid oligomer (14). Therefore, it can be said that only AN can be polymerized by TEP. The electron density of the β-carbon of other monomers is not as low as that of AN, and the addition of monomeric and dimeric Zwitterions to monomers seem to be difficult.
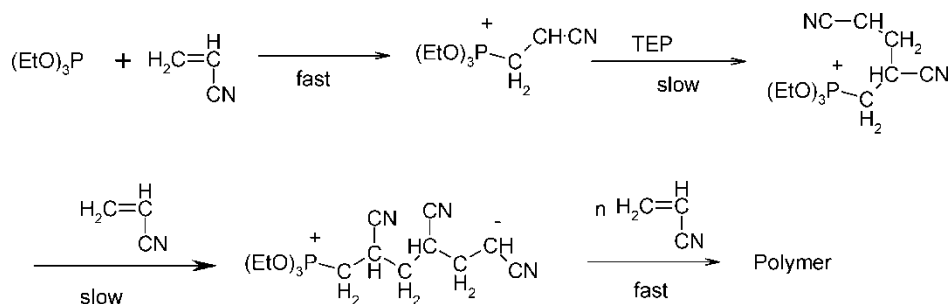
Scheme 4. Polymerization of AN initiated with TEP.

Table 2
Effect of addition of monomer during the polymerization

Run	[P(OEt)$_3$] (mole/L)	[AN]$_0$ (mole/L)	[AN]$_a$	[NBu$_4$Br] (mole/L)	Polymerization time (h)	Yield (%)	Mw × 10^{-3}	Mn × 10^{-3}	PD, Mw/Mn
7-1	0.006	3.19	—	0.033	2.8	65	141	63	2.2
7-1a	—	—	5.28	—	3 + 0.8	—	160	70	2.3
7B-1	0.006	3.19	—	0.033	1.6	26	108	50	2.2
7B-2	”	”	—	”	2.1	71.5	157	69	2.3
7B-3a	—	—	5.28	—	2.2 + 2.8	—	230	95	2.4
30-1	0.005	5.28	—	0.027	0.7	56	119	54	2.2
30-2	”	”	—	”	2.0	89	156	68.3	2.3
30-3a	—	—	5.28	—	3.5 + 2.5	—	167	73	2.3
30-4	—	—	”	—	3.5 + 3	—	172	74.5	2.3
30-5	—	—	”	—	3.5 + 17	—	270	109.5	2.5

7-1a and 7B-3a: 4 mL of additional AN were added to the initial system (4 mL AN + 15 mL DMF) after 3 and 2.2 h, respectively. 30-3a: 8 mL of AN and 15 mL of DMF were added after 3.5 h to the initial system (8 mL of AN and 15 mL of DMF).

Table 3
Polymerization of AN with phenyldiethoxyphosphine (PEP)

	Run				
	19	27-1	27-2	28A-1	28A-2
[A], mol/L	5.05	5.05	5.05	5.06	5.06
[PEP], mol/L	0.017	0.01	0.01	0.007	0.007
[NBu$_4$], mole/L	0.041	0.041	0.041	0.041	0.041
Mn calcd., $\times 10^{-3}$	15.5	25.8	25.8	38.7	38.7
Polymerization time, h	4	2	4	2	4
Yield (%)	96	76	86	74	88
Mw $\times 10^{-3}$	162	169	174	134.2	166
Mn $\times 10^{-3}$	70.5	73.2	75	60	72
PD, Mw/Mn	2.3	2.3	2.3	2.2	2.3

Figure 3 shows FTIR spectra of a copolymer (sample 2). The peak due to the carbonyl group of methylacrylate unit is clearly observed. Elemental analysis of copolymers revealed that 1 MA unit is included for each 10 AN units.

Conclusions

From the above results, it was confirmed that TEP is the only anionic initiator, which gives PAN with high molecular weight in DMF giving solutions ready for spinning fibers. Substitution of ethoxy groups with phenyl group decreased the molecular weight. However, the solutions of high molecular weight PAN were not stable, and the solution became gel on standing for a few days due to the dipole-dipole interaction between the nitrile groups. It was necessary to add more solvent and to stir on heating in order to dissolve the PAN gels. Although the propagating anion is a living anion during the polymerization,

Table 4
Polymerization of AN with diphenylethoxyphosphine (DPP)

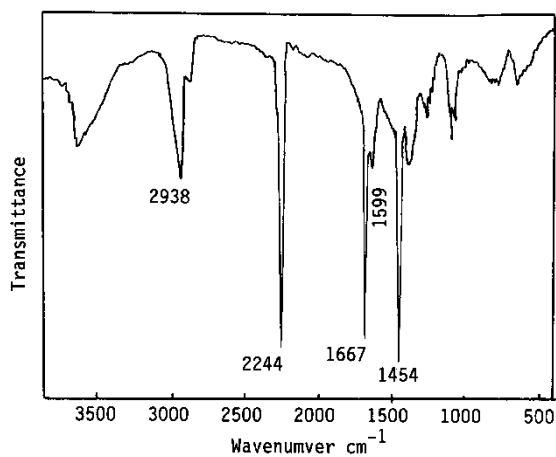|	Run	
	14	15
[AN], mole/L	5.01	5.05
[DPP], mole/L	0.046	0.015
[Nbu$_4$Br], mole/L	0.041	0.093
Mn calcd., $\times 10^{-3}$	5.8	17.4
Polymerization time, h	3	4
Yield, %	95	82
Mw $\times 10^{-3}$	64	105
Mn $\times 10^{-3}$	52	48
PD, Mw/Mn	2	2.2

Figure 2. FTIR spectra of polyAN obtained with DDP.

Table 5
Copolymerization of AN with MA using TEP initiator

Run	[AN]	[MA]	Polym. time (h)	Yield (%)	Mn	Mw	PD
1	4.81	0.18	47	32	19000	35500	1.8
2	4.55	0.37	23.5	21	36800	76400	2.1
3[a]	4.05	0.73	24	1.6	—	—	—
4[a]	3.50	1.10	24	1.4	—	—	—

[TEP] = 0.008 M, [NBu$_4$Br] = 0.016, at room temperature.
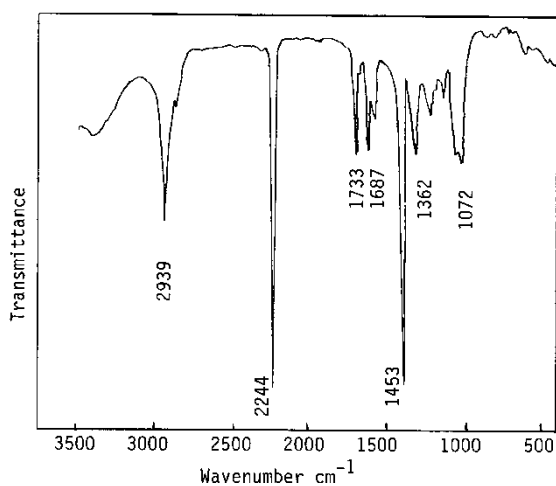[a]No polymer was isolated.

Figure 3. FTIR spectra of poly(AN-*co*-MA) (copolymer 2) initiated with TEP.

exact control of molecular weight is difficult because the initiation is much slower than the propagation, and also due to inevitable chain transfer reaction. The rather broad molecular weight distribution is attributed to the slow addition of the monomeric and dimeric Zwitterions to AN, the reaction of propagating anion with the nitrile groups, and also to the trace of moisture, which could not be removed completely from the polymerization system. However, it is possible to obtain very high molecular weight PAN if a completely dry inert polymerization system could be achieved.

The copolymerization of AN with MA was possible, although the molecular weight was not high.

Acknowledgements

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