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Synthesis of Poly(N,N-Dimethylaminopropylacryl Amide-g-Acrylic Acid) and Crosslinking of its Trunk Sequence

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Summary

The graft copolymers composed of weak base and weak acid sequences, i.e., poly(N,N-dimethylaminopropylacryl amide-g-acrylic acid) (poly(DAPA-AA)) including 51-87 mol% of acrylic acid (AA) were prepared by redox system using cerium(IV) ammonium sulfate as initiator. Microphase separation of two sequences was observed in basic casting solvent. The crosslinking of DAPA sequence, which had shown spheric morphology, was carried out by mean of gas-solid phase quaternization reaction with 1,4-dibromobutane. The reaction product was soluble in NaOH aq. or HCl aq. until 4.3% quaternization of DAPA unit without remarkable increase of intrinsic viscosity. And they were found to be very different in solubility from the raw graft copolymer.

Introduction

The crosslinking reaction of the trunk sequence of graft copolymer is interesting from following two points.

As well known, in the selective solvent (non or poor for trunk and good for branch), or in some cases in solid state, trunk sequences form very small isolated spheric domains. Under these conditions, it can be expected to obtain a soluble microgel (crosslinked polymers sufficiently small as to dissolve in suitable solvents) by the crosslinking reaction of the trunk sequence. The possibility had been suggested in the course of the crosslinking reaction of block copolymer in our previous papers (1,2), and this type of polymer could reacently be prepared successfully by quaternization crosslinking of poly(4-vinylpyridine-g-styrene) in the mixed solvents (3). Bendnar and his colaborators reported also in a recent paper (4) that they had obtained the polymer composed of a crosslinked core and branches (shell) by the fast electron irradiation crosslinking of poly[styrene-b-(ethene-co-butene)-b-styrene] in solution.

On the other hand, if these crosslinked materials are obtained, many practical applications are expected; mixing of anionic and cationic polymers without the polyion complex formation, the introduction of micro heterogeneity in polymer matrix, preparation of emulsion or suspension with very small particles etc..

In this study, the graft copolymer, poly(N,N-dimethylaminopropylacryl amide-g-acrylic acid) was prepared, and microphase separation was observed when the polymer was cast from a basic aqueous solution. Then, the sample which showed spheric PDAPA texture was cast under the same conditions as in the observation of microphase separation. Quaternization of PDAPA sequence was carried out in a film state by gas phase with 1,4-dibromobutane to examine the above described expectation. If Tg of the graft copolymer or crosslinked product is sufficiently high to maintain the texture during the reaction, we can expect to obtain a soluble product.

Experimental

Polymer Synthesis: The procedure of graft coplymers and microgels syntheses can be expressed schematically as following:

Polyacrylonitrile(PAN) or
Poly(acrylonitrile-co-vinylacetate)(P(AN-VAc))
↓ Amidation
(N,N-dimethyl-1,3-diamino-n-propane)(DAP)
Poly(3-dimethylamino-n-propylacryl amide)(PDAPA) or
Poly(3-dimethylamino-n-propylacryl amide-co-vinylalcohol)
(PDAPA-OL)
↓ Graft copolymerization
(acrylic acid, HNO_3, Ce^{+4})
Products
↓ Separation
Graft copolymers; poly(DAPA-AA)
↓ Crosslinking ($BrCH_2CH_2CH_2CH_2Br$)
Soluble microgel

*(the reason to introduce this monomer is mentioned in a following paragraph and in discussion)

1st step. PAN and P(AN-VAc) were prepared by the usual emulsion polymerization at room temperature (initiator: $K_2S_2O_8$-$Na_2S_2O_3$). The monomer ratio (VAc(mol)/AN(mol)) was 0.03. Even though PDAPA itself has the active sites to form radicals by Ce^{+4}, VAc was copolymerized to introduce -OH group which is the effective radical source in this redox system. Conversion of AA during graft copolymerization was compared for PDAPA and PDAPA-OL.

2nd step. PDAPA and PDAPA-OL were prepared by the reaction of PAN or P(AN-VAc) in DAP containing a small amount of water (5) at refluxing temperature of the solvent (about 110 °C) for 30 or 13hr respectively. The solvents of the reaction solution were removed completely by the distillation and evacuation, and then, polymer was dissolved again in benzene/dioxane mixture (v/v:2/1). This solution was dropped into benzene under vigorous stirring. Precipitated polymer was separated by decantation and dried on Teflon dish.

3rd step. Graft copolymer poly(DAPA-AA) was synthesized by the following manner. PDAPA or PDAPA-OL, concentrated nitric acid, AA monomer distilled before use were dissolved in water (total volume:500 ml). Cerium(IV) ammonium sulfate: $(NH_4)_4Ce(SO_4)_4.2H_2O$ (CAS) in 50 ml diluted nitric acid (pH 1) was dropped into this mixture for several times under nitrogen atomosphere at room temperature. A 50 ml portion of solution was taken from the reaction solution just before the addition of CAS solution. pH of the reaction solution was 3.5-4.0 during the graft copolymerization. The collected sample solutions were filtered and adjusted to pH 1. The precipitate (PAA) was separated by decantation. And then, pH of the solution was changed stepwise from pH 3 to 8 by adding aqueous ammonia. At each step of pH change by 1, polymer precipitated from the solution was separated by centrifuge (3500 r.p.m., for 10 minutes). All products precipitated at pH 3-8 from one sample were gathered, washed, and dried. Other detailed conditions of graft coploymerization are shown in Table 2.

Characterization: Molecular weight of PAN and P(AN-VAc) was determined by viscometric measurement (6) ($[\eta]=2.43\times10^{-2}\overline{Mv}^{0.75}$; in dimethylformamide, at 25 °C). The same intrinsic viscosity-molecular weight relation of PAN was applied to P(AN-VAc) considering low content of VAc unit in the copolymer. The content of VAc in P(AN-VAc) and the composition of graft copolymer were determined by referring IR spectrum of PAN and poly(vinyl acetate) blend or PDAPA and PAA blend. The details of this method had been described in a previous paper (7).

The formation of graft copolymer was confirmed by the turbidimetry. 1 ml of sample solution (polymer concn.:0.3-0.5%) and 2 ml of conc. nitric acid (12N) were dissolved in 50 ml water, and then, aqueous sodium hydroxide (1N) solution was added stepwisely with vigorous stirring in a cell for turbidity measurement (cylindric Pyrex cell, 200 ml). At each step, pH (model HM-7E, Toa Electronics Ltd.), temperature, and the turbidity (single beam HITACHI Spectrophotometer 124) of the solution were measured.

Electron Microscopy: Poly(DAPA-AA) was dissolved in aqueous ammonia (pH 11, polymer concn. 0.8wt%). Preparation of the specimen by using this solution was same as that reported in a previous paper (7). Morphology of the domains was observed by electron microscope (HITACHI-HS-7). Several examples of the micrographs were shown in Figure 4.

Crosslinking of PDAPA Sequence: Sample no. 19 was dissolved in ammonia solution (pH 11, polymer concn. 8wt%), cast on Teflon sheet. Solvent was evaporated slowly and then dried in vacuum at room temperature. Crosslinking was carried out by exposing films to 1,4-dibromobutane gas at 90 °C under nitrogen flow. After the reaction was over, films were washed with acetone and dried. The degree of quaternization was determined by Volhaldt's titration method. In the case of the insoluble products, titration was carried out after the samples were swollen sufficiently in nitric acid. Other quaternization conditions are shown in Table 3 along with the results.

Viscometry: Viscosity of quaternized products was measured in the water containing NaCl (0.887mol/l) and NaOH (0.213N) at 30 °C.

Results and Discussion

Polymer Synthesis: The characters of PAN and P(AN-VAc) were summerized in Table 1. VAc content was 4.8 mol%.

IR spectra of PDAPA and PDAPA-OL were shown in Figure 1. The absorption at 2240 cm^{-1}(nitrile group) in PAN or P(AN-VAc) vanished perfectly and the absorption at 1230 cm^{-1} responsible to amide group appeared in them. And the absorption at 1730 cm^{-1} (ester group) disappeared. According to these results, amidization and hydrolysis were almost 100%.

The result of the turbidimetry was shown in Figure 2. In the case of the mixture of PDAPA and PAA, appreciable turbidity could not be observed through out all pH range. While in the case of the products considered as the graft copolymer, the distinct turbidity was observed between pH 3 and pH 8. Thus the graft copolymer formation was confirmed, and AA content of them was 51-87 mol%. In Figure 3, AA content of the graft copolymers increased with the reaction time. The increase of AA content was strongly affected by Ce^{+4} concentration, and slightly more rapid in the case

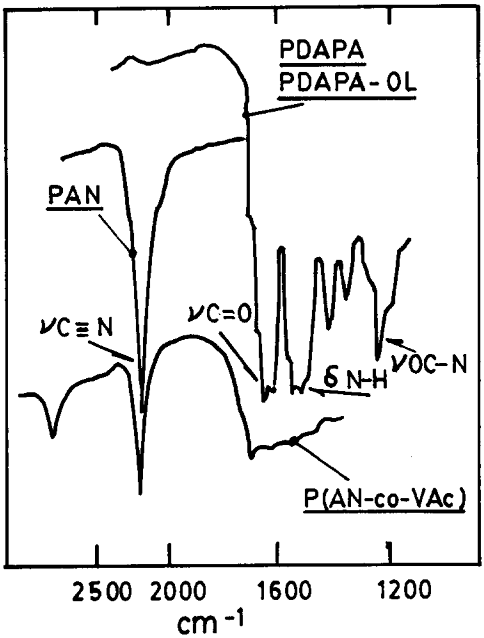


Figure 1. IR spectra of the basic trunk polymers and raw polymers.

of PDAPA-OL than in the case of PDAPA (from the comparison of series c with series e). As a conclusion, this well known redox system is convenient to prepare the graft copolymer, poly(DAPA-g-AA).

Electron Micrograph: The typical electron micrographs of the graft copolymers are shown in Figure 4. In some cases, lamellar like texture was observed, but PDAPA sphere in a PAA matrix was observed in most cases.

Degree of Quaternization and Viscosity: The degree of quaternization, intrinsic viscosity, soluble pH range of the products were shown in Table 3.

The decrease of intrinsic viscosity was observed at the first stage of the quaternization reaction (until 3.3 mol% of 4VP unit). This result differs from that obtained by Bendnar et al (4) which showed a regular increase of molecular weight during the crosslinking by high energy electron irradiation, and suggests that the intermolecular crosslinking of PDAPA did not occur at the first stage of the reaction. However, when the degree of quaternization reached to 12% of DAPA unit, macrogelation occurred partially in the reaction system. At this time the white small spot appeared on the film.

Table 1
Preparation of basic trunk polymers.

Reaction conditions				Yield	M
polymer	(g)	amine (g)	temp (°C)	(g)	$\times 10^{-5}$
PAN	43.5	425	125.5	38.1	11.5
P(AN-VAc)	43.2	425		31.3	6.4

PAN: $Mv = 3.9 \times 10^5$, P(AN-VAc): $Mv = 2.2 \times 10^5$, number of VAc unit/number of AN unit=0.048. Molecular weight M of trunk polymer was estimated from these of raw polymers and supposing quantitative amidation.

Amine: N,N-dimethylamino-n-propane diamine.

Other reaction conditions: $[amine]/[-CN] = 5/1$, $[H_2O]/[-CN] = 1/1$.

The variation of intrinsic viscosity as a function of the degree of quaternization is shown in Figure 5. Intrinsic viscosity increased rapidly when the degree of quaternization exceeded 4.3 mol%. We can suppose that the intermolecular crosslinking had occured after this conversion.

Other remarkable points exist in Table 3. 1) The quaternized PDAPA homopolymer formed macrogel and became insoluble at any pH range in

Table 2.

Conditions of copolymerization and composition of products

	reaction conditions				
sample no.	trunk polymer	$\frac{[AA]}{[DAPA]}$	[I] $\times 10^3$	reaction time (hr)	mol% of AA in products[b)]
1	PDAPA	0.64	6.0[a)]	2	52
2			9.1	2	57
3			17.0	2	73
4		0.77	3.9	3	51
5			4.4	2	73
6			5.9	22	81
7		0.87	10.0	2	82
8			14.0	2	-
9			25.0	2	87
10	PDAPA -OL	0.64	5.6	2	-
11			8.4	2	-
12			17.0	2	75
13		0.73	4.3	2	-
14			5.0	2.5	77
15			6.5	2	81
16		0.88	9.4	2	86
17			10.4	2	87
18			23.0	2	87
19		0.83	10.0	4	80

a) The conditions of this run mean that copolymerization was carried out: initiator concentration 6.0×10^{-3} (mol/l) for 2hr at first, then 9.1×10^{-3} for 2hr, and finally 17.0×10^{-3} for 2hr.

b) Determined by IR spectra (see Experimental).

Initiator: $(NH_4)_4Ce(SO_4)_4\cdot 2H_2O$. pH of the solution: 3.5-4.0. Polymer concentration: 24.3-30g/500 ml solution (50 ml of the solution was sampled just before the second or third addition of initiator solution). Yield of the graft copolymer was about 30-40 wt% of trunk polymer (this low yield was mainly attributed to the good adhesion of the copolymer to glass vessel).

water. The graft copolymers, even though more quaternized than PDAPA, were still soluble. 2) The pH range where the quaternized graft copolymer was insoluble changed toward acidic side as the degree of quaternization increased. 3) The intrinsic viscosity of quaternized graft copolymers did not change appreciably until 4.3 mol% of the degree of quaternization.

From these results, following considerations and suppositions are to be adopted; PDAPA domains in the film no. 3, 4, and 5 are sufficiently crosslinked, as to form macrogel if they belong to the homopolymer. The crosslinking closed to only a spheric domain certainly occurred in the graft copolymer at the first stage of the reaction.

The quaternized products have the structure composed of a crosslinked core, and PAA branches sorrounding this core. Then the solubility of the graft copolymers, dominated by sorrounding branches, became similar to PAA.

As a conclusion of this study, it is possible to prepare the soluble

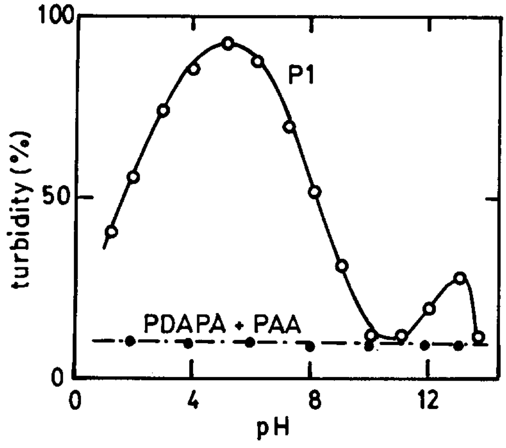


Figure 2. Turbidimetric titration of poly(DAPA-g-AA) P1 and PDAPA-PAA mixture.

Polymer concn.; 0.06g/ℓ

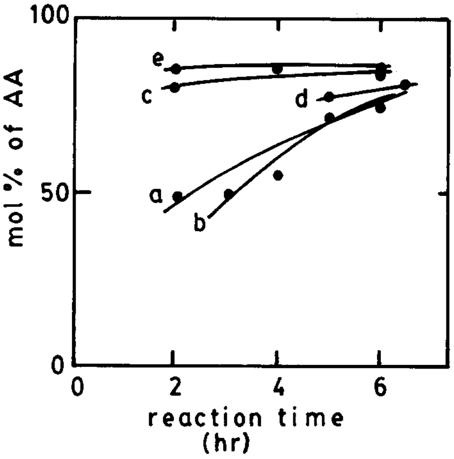


Figure 3. Increase of AA unit in graft copolymers with reaction time.

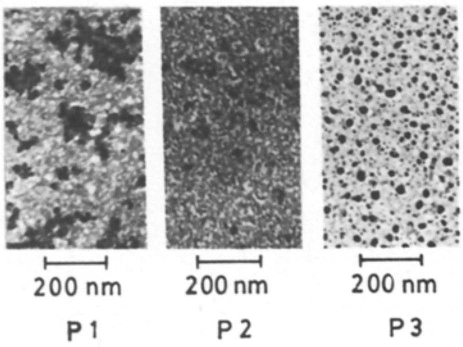
a; sample no.1,2,3. b; no.4,5.
c; no.7,9. d; no.14,15.

Table 3.

Crosslinking of trunk sequence by quaternization reaction and characters of the products.

	reaction conditions		results		
film no.	d a) (µm)	reaction time (hr)	d.q. b) (DAPA %)	[η] c) (mℓ/g)	insoluble pH range
0	-	0.0	0.0	1.4×10^2	3-9
1	100	8	1.5	1.3 "	0-5
2	130	15	3.3	1.1 "	-
3	80	15	3.9	1.2 "	0-4
4	106	30	4.3	1.6 "	0-2
5	100	70	12.0	-	- e)
1' d)	80	2.0	3.8	-	insoluble
2'	85	4.0	7.7	-	"

Other reaction conditions: in dibromobutane vapor, at 90 °C.
a) film thickness. b) degree of quaternization, measured by Volhald's method. c) solvent: NaOH 0.213N, NaCℓ 0.887moℓ/ℓ, 30°C. d) quaternized PDAPA homopolymer. e) partially insoluble in whole pH range.



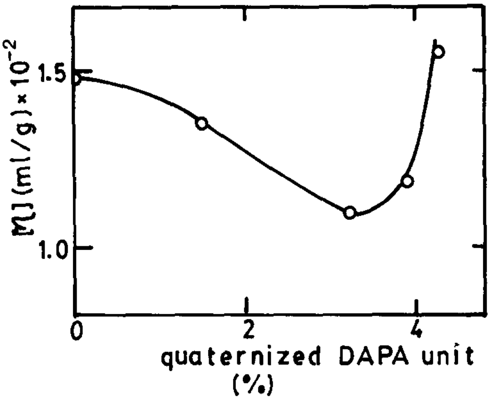


Figure 4. Electron microscopic observation of the graft copolymer films cast from aqueous ammonia.

P1; sample no.4, P2; sample no.14, P3; sample no.19, respectively.

Figure 5. Intrinsic viscosity of crosslinked polymers.

In 0.213N NaOH/0.887mol NaCℓ, at 30 °C.

polymer composed of a crosslinked core and branches by solid-gas phase crosslinking of the trunk sequence of a graft copolymer. And the soubility of it is dominated mainly by the solubility of the branches.

References

1) K. Ishizu, K. Bessho, T. Fukutomi, T. Kakurai, Macromolecules 16, 13 (1983)
2) K. Ishizu, K. Inagaki, K. Bessho, T. Fukutomi, Makromol. Chem., 185, 1169 (1984)
3) T. Fukutomi, R. Saito, K. Ishizu, J. Polymer Sci., to be submitted
4) B. Bendnar, J. Devaty, B. Koupalova, J. Kralicek, Polymer, 25, 1178 (1984)
5) S. Dragan, I. Petrarieu, M. Dima, J. Polymer Sci., Polym. Chem. Ed., 19, 2881 (1981)
6) H. Malmgren, Acta Chem. Scand., 6, 1 (1952) : J. Brandrup, E. H. Immergut Ed., Polymer Handbook 2nd Ed., IV-9, A WILEY-INTERSCIENCE PUBLICATION (1975)
7) T. Fukutomi, T. Horikoshi, Koji Ishizu, Polymer J., 16, 619 (1984)
8) K. Ishizu, K. Inagaki and T. Fukutomi, J. Polymer Sci., Polym. Chem. Ed., 23, 1099 (1985)

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