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Preparation and Properties of Polyaniline Nitrile-Rubber Copolymers

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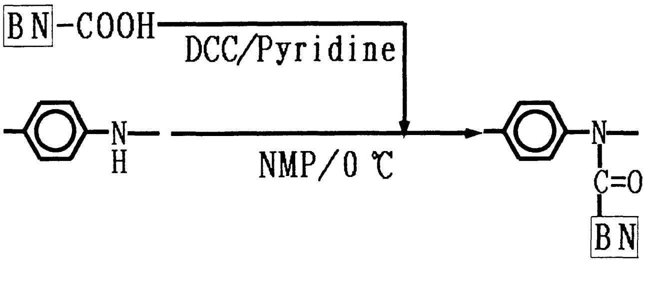
Graft copolymers of polyaniline and telechelic nitrile rubber have been synthesized. They were soluble in N-methyl-2-pyrrolidone(NMP) and flexible self-supporting films were obtained by casting the solutions. Upon protonic doping, their conductivities rised from 10^{-8} to 10^{-2} S/cm. Spectroscopic, electrochemical and mechanical studies demonstrated that the electronic states of copolymer are fundamentally the same as those of the original polyaniline, *i.e.* , they are not much influenced by the grafting, however, the mechanical properties are affected by rubber.

Polyaniline(PAn) has been attracted much attention among various conducting polymers, because the conducting form of PAn exhibits excellent chemical stability and relatively high electrical conductivity. Recently, a soluble PAn in NMP has been synthesized and the PAn film has been obtained by casting from the NMP solution.1) Also a PAn gel has been prepared from the soluble PAn.2)

On the other hand, the reduced PAn is well soluble in amide solvents, and it can be regarded as an aromatic secondary amino compound. Hence it is possible to apply a replacement reaction at the N position in the PAn main chain. N-acylation and N-alkylation of the reduced PAn have been reported by the author.3)

In this letter, we report a preparation of novel graft copolymers comprised of PAn as the main chain and of a nitrile rubber as the side chains and their properties.

PAn used was synthesized by oxidative polymerization of aniline, which was carried out utilizing ammonium peroxodisulfate as the oxidant in an acidic solution at 0 °C for 6 hours. PAn obtained was



DCC : dicyclohexylcarbodiimede
BN-COOH : Telechelic nitrile rubber, acrylonitrile content 17 mol%

Fig. 1. Partial structure of graft copolymer and reaction scheme for formation of polyaniline graft copolymer.

Table 1. Yield of graft reaction and conductivity of graft copolymers

No.	Nitrile rubber/g	(NH/mol%	wt%)	yield/%	Conductivity/S cm^{-1} undoped	doped
1	3.95	(10.0	80)	96	2.7×10^{-8}	1.6×10^{-2}
2	1.98	(5.0	66)	98	1.5×10^{-8}	8.7×10^{-2}
3	0.99	(2.5	50)	97	1.2×10^{-8}	2.6×10^{-1}

undoped by 2 mol dm^{-3} aqueous ammonia to get a soluble PAn, and was reduced with an aqueous hydrazine under the nitrogen atmosphere. The molecular weight(Mn) was 12000(measured by GPC).

The graft reaction was carried out with the following method. The telechelic nitrile rubber supplied from Goodrich Co. was used. It is a butadiene-acrylonitrile random copolymer, which has one carboxyl group at the terminal and the acrylonitrile of 17 mol% in content. Its Mn was 3600. This nitrile rubber was dissolved in pyridine and added twice the molarity of dicyclohexylcarbodiimide at 0 °C with stirring for 2 hours. Then, the NMP solution of reduced PAn was added to the solution, continued the stirring for 4 hours at room temperature to carry out the graft reaction. The partial structure and synthetic scheme are shown in Fig. 1. The reaction mixture was then poured into about 10 times of methanol and the precipitate was collected, undoped by 2 mol dm^{-3} aqueous ammonia and dried under vacuum.

The ratio of carboxyl groups at the terminal of nitrile rubber to the NH groups of the reduced PAn in the graft copolymer was controlled over a range of 1 mol% to 10 mol%. This graft reaction(N-acylation) was confirmed by IR spectra(2237 cm^{-1} assigned to nitrile group and 1650 cm^{-1} assigned to amide carbonyl). The yield of this reaction is given in Table 1.

The solubility of obtained copolymers were listed in Table 2. They were well soluble in the NMP-hydrazine mixtures. And these solutions were cast on a teflon plate and dried at 80 °C. Self-standing films were obtained from all graft copolymers. Those in the range of 10 mol% through 2.5 mol% were flexible, while that of 1 mol% was brittle.

Table 2. Solubility of graft copolymers and original PAn[a)]

Solvent	Solubility(pure/hydrazine added) 1	2	3	PAn
Xylene	is/ss	is/ss	is/ss	is/is
THF	ss/ss	is/ss	is/is	is/is
Dichloroethane	ss/ss	is/ss	is/ss	is/is
Pyridine	ss/ss	is/ss	is/ss	is/is
DMAc	ss/s	ss/s	s/s	s/s
NMP	ss/s	s/s	ss/s	s/s
HMPA	ss/s	s/s	s/s	s/s

a) is:insoluble, ss:slightly soluble, s:soluble
THF:tetrahtdrofurane, DMAc:N,N-dimethylacetamide
NMP:N-methyl-2-pyrrolidone HMPA:hexamethylphosphric triamide
The number in this table corresponds to the copolymer of the same number in Table 1.

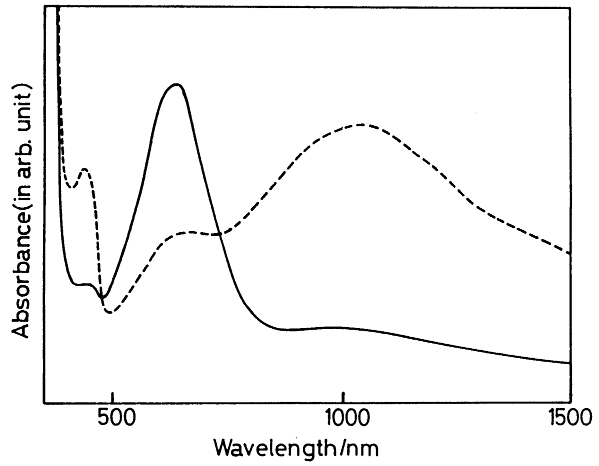


Fig. 2. Absorption spectra of doped(dotted line) and undoped(solid line) graft copolymer.

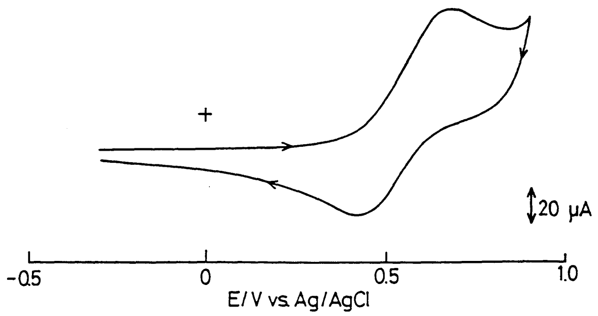


Fig. 3. Cyclic voltammogram of graft copolymers.

The UV spectra of undoped and HCl doped 10 mol% composition films were shown in Fig. 2. These spectra were similar to those of undoped and doped PAn. This indicates the existence of active PAn structure in the copolymer despite of the N-acylation at the PAn main chain.4)

Cyclic voltammetric curve of the 10 mol% composition film on an ITO glass, which was recorded in 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate between −0.3 and 0.8 V vs. Ag/AgCl, supported that this copolymer is an electroactive polymer. It was also similar to that of PAn in non-aqueous solvent.5) In Fig. 3, the value of the potential separetion between the peaks suggest that the reduction and oxidation kinetics which are limited by a slow ion diffusion in the film and/or a slow electorn transfer may be different. The peak-to-peak separation did not change after 50 times of the scanning.

The conductivities of undoped and doped films measured by two-probe method and four-probe method, respectively are shown in Table 1. Surprisingly, the 10 mol% composition film shows conductivity as high as 10^{-2} S/cm, in spite of large content of the nitrile rubber(80 wt%) in the graft copolymer. The electronic structure of main chain is considered to be modified by the acylation of about 10% of N positions in the original PAn.

Thermogravimetric analysis of the undoped 10 mol% composition copolymer shown in Fig. 4, indicated that this copolymer is stable up to near 300 °C in air with an initial weight loss of 0-5%. This behavior was unexpectable in view of the fact that the copolymer contains 80 wt% of the nitrile rubber.

Table 3. Comparison of mechanical properties of between polyaniline and graft copolymer

		Elastic modulus/GPa	Tensile strength/MPa	Breaking elongation/%
PAn	undoped	1.15(0.06)	50 (10)	14(4)
	doped	1.25(0.08)	39(7)	10(3)
1a)	undoped	0.014(0.003)	2.9(0.7)	49(9)
	doped	0.011(0.002)	2.8(0.8)	73(20)

a) 1 corresponds to copolymer in Table 1.

Table 3, given a comparison of mechanical properties between the copolymer containing 80 wt% the nitrile rubber and the original PAn, shows that the elastic modulus and the tensile strength of copolymers are remarkably lower but the breaking elongation is larger than those of PAn, by introducing the rubber into PAn.

From these results, it might be concluded that the electrochemical and the thermal properties of graft copolymer are mainly governed by the properties of main chain of polyaniline. However, the mechanical properties are governed by the nitrile rubber.

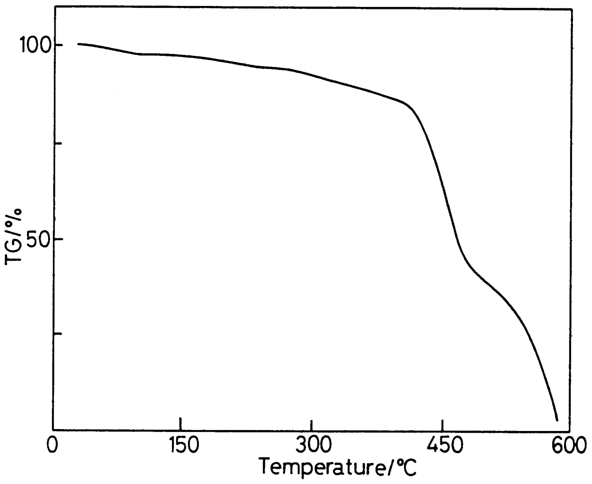


Fig. 4. Thermogravimetric analysis curve of graft copolymer.

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