Copolymers of N-Vinylcarbazole with Monomers Containing Carboxylic Acid Groups or Carboxylic Anhydride Groups. I

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SYNOPSIS

N-Vinylcarbazole has been copolymerized with olefinic monomers possessing carboxylic acid or carboxylic anhydride functionality to yield copolymers with associated solubility in aqueous alkaline media. The copolymers were prepared to be part of a photoconductive lithographic printing plate assembly. The composition of the copolymers and the reactivity ratios have been evaluated. Copolymerization mechanisms are discussed. Alkali solubility has been measured in terms of the decoating speeds of films of the copolymers from aluminum plates. The major aim of producing an alkali-soluble copolymer that retained the photoconductive properties associated with poly(N-vinylcarbazole) was achieved in part.

INTRODUCTION

Poly(N-vinylcarbazole) (PVK) has been extensively used in recent years in the reprographics industry as a photoconductive polymer.[1-6] Copolymers containing monomeric carbazole groups appear to be of greater utility in the investigation of physical properties associated with PVK. Examples of this include the work of Turner, Miyashita, and others on copolymers of N-vinylcarbazole with comonomers such as p-styrenesulfonate, diethylfumarate, and diethyl azodicarboxylate in the investigation of singlet or triplet quenching in PVK analogues.[7-9]

Copolymers of N-vinylcarbazole (NVK) with alkali-soluble monomers have received scant attention apart from the work concerning poly(N-vinylcarbazole-co-maleic anhydride) and the copolymerizations of NVK with acrylic acid carried out by Chapiro.[10-13] Elsewhere, Mulvaney et al. used acryloyl chloride as a comonomer with NVK. However, the resulting copolymer was used for the attachment of electron acceptors rather than for any inherent alkali solubility.[14,15]

Direct functionalization of poly(N-vinylcarbazole) to give an alkali-soluble homopolymer has proved difficult.[16] Several groups have sulfonated the polymer, but only in order to attach sensitizing dyes.[17,18]

EXPERIMENTAL

Reagents

N-Vinylcarbazole was supplied by Howson Algraphy Ltd (Leeds). Prior to use, it was purified by recrystallization from ligroin (60–80°C) and was dried in vacuo at 35°C. The initiator, azobis(isobutyronitrile) (AIBN), was supplied by BDH (Poole) and was recrystallized twice from methanol. The reaction solvent, tetrahydrofuran, was distilled over lithium aluminum hydride.
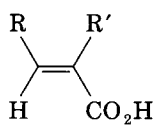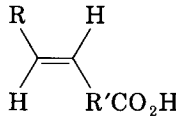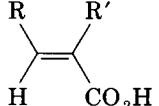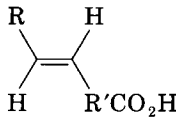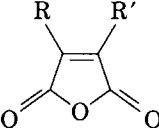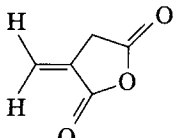
The monomers used in copolymerizations with NVK are listed in Table I. Purification of these materials was carried out as indicated in Table II. Fumaric acid was used as supplied by Fluka, London.

Bulk Copolymerization Procedure

All copolymerizations were carried out following the method of Chang et al.[15] The required volume of dry tetrahydrofuran was purged with nitrogen for 10

Table I   Monomers Used in Copolymerizations with NVK

Comonomer	R	R'	Name	Supplier
	H	H	Acrylic acid	BDH
	H	Me	Methacrylic acid	BDH
	Me	H	Crotonic acid	BDH
	Et	H	trans-2-Pentenoic acid	Howson Algr.
	Pr^n	H	trans-2-Hexenoic acid	Howson Algr.
	H	CH_2	Vinylacetic acid	Howson Algr.
	H	$(CH_2)_2$	4-Pentenoic acid	Howson Algr.
	COOH	H	Fumaric acid	Fluka
	H	CH_2COOH	Itaconic acid	Howson Algr.
	CH_2COOH	H	Glutaconic acid	Howson Algr.
	CH_2COOH	H	trans-3-Hexenedioic acid	Howson Algr.
	H	H	Maleic anhydride	Fluka
	Me	H	Citraconic anhydride	BDH
	—	—	Itaconic anhydride	BDH

Table II   Purification of Reactants

Monomer	Recrystallization Solvent	Distillation T (°C)	p (mm Hg)
Acrylic acid	—	32–34	3
Methacrylic acid	—	60–61	3.5
Crotonic acid	Ligroin (60–80°C)	—	—
Vinylacetic acid	—	88–90	10
Itaconic acid	Acetone	—	—
Itaconic anhydride	Dichloromethane	—	—
4-Pentenoic acid	—	80	10
trans-2-Pentenoic acid	—	100	2.5
trans-3-Hexenedioic acid	Tetrahydrofuran	—	—
Glutaconic acid	Dichloromethane	—	—
Maleic anhydride	Toluene	—	—
trans-2-Hexenoic acid	—	105	3.5
Citraconic anhydride	—	83–84	2.5

min. The reagents were quickly added, and the resulting solution further purged with nitrogen for 10 min. The total monomer concentration in each case (i.e., concentration of NVK + concentration of comonomer) was $1.0M$. The free radical initiator, AIBN, was used at a constant level of 0.5 mol % of the total monomer concentration. Initially, molar feed ratios (NVK–comonomer) of 1 : 1, 2 : 1, 4 : 1, and 10 : 1 were used. For copolymerization of NVK with acrylic acid, this range was later extended to include 1 : 10, 5 : 1, and 2 : 1 ratios; i.e., rich in acrylic acid. The reaction time in all cases was 18 h at 64°C.

After the reaction the solutions were allowed to cool to room temperature and were precipitated, with vigorous stirring, in a four times volume excess of ligroin (60–80°C). The resulting material was filtered and dried at 50°C in air. Homopolymeric PVK was exhaustively Soxhlet extracted with boiling toluene. The homopolymeric acidic polymers were removed with boiling water.

Copolymer Evaluation

The successful formation of copolymer was demonstrated by infrared spectroscopy using a Pye Unicam SP1100 IR spectrophotometer. The carboxylic acid groups absorbed at approximately 1710 cm^{-1} and the anhydride groups at 1850 and 1780 cm^{-1}. Carbazole absorptions were observed at 745 and 720 cm^{-1}. It should be recalled that exhaustive extraction procedures were carried out on the initial reaction products, thus ensuring the removal of homopolymeric species.

Tetrahydrofuran (THF) solutions of the copolymers (30 mg/dm^3) were examined for their carbazole absorptions at 330 and 344 nm, using a Pye Unicam SP8-150 spectrophotometer and also for fluorescence using a Perkin-Elmer LS5 fluorimeter.

Molar mass values and polydispersity ratios for the copolymeric products were determined by size exclusion chromatography courtesy of R.A.P.R.A., Shawbury, Shrewsbury, Shropshire, and also of Howson Algraphy (U.K.) Ltd., Leeds. Tetrahydrofuran was used as the eluting solvent.

Copolymer compositions were evaluated by nonaqueous titration of the acidic groups. Using a value for the extinction coefficient of copolymerized vinylcarbazole of 3.326×10^3 cm^2/mol for its 344-nm absorption, good agreement was generally found between the two sets of results. In this way relationships between molar feed ratios and copolymer compositions were derived, as were reactivity ratios for several of the comonomer pairs.

Coating Procedures and Associated Alkali Solubility

Assessment of the alkali solubility of copolymer films was determined as follows: A solution of copolymer (10% w/w) containing 0.1% of a sensitizing dye and 0.1 g of dodecylamine were made up in a

Table III   Copolymerization of NVK with Carboxylic Acids and Anhydrides

Molar Feed Ratio (NVK–Comonomer)	1 : 10	1 : 5	1 : 2	1 : 1	2 : 1	4 : 1	10 : 1
Comonomer	Nature of Isolated Products[a]						
Acrylic acid	Co	Co	Co	Co	Co	Co	Co
Methacrylic acid	Co	Co	Co	Co	Co	Co	Co
Crotonic acid				Co	Co	Co	Co
trans-2-Pentenoic acid				(Co)	(Co)	(Co)	H
trans-2-Hexenoic acid				(Co)	H	H	H
Vinylacetic acid				(Co)	(Co)	H	H
4-Pentenoic acid				(Co)	(Co)	(Co)	(Co)
Fumaric acid				Co	Co	Co	Co
Itaconic acid	Co	Co	Co	Co	Co	Co	Co
Glutaconic acid				Co	Co	(Co)	(Co)
trans-3-Hexenedioic acid				A	A	A	(Co)
Maleic anhydride				Co	Co	Co	Co
Citraconic anhydride				Co	Co	Co	Co
Itaconic anhydride				Co	Co	Co	Co

[a] Co, copolymer; (Co), copolymer 5% yield; H, PVK; A, homopolymeric acid.

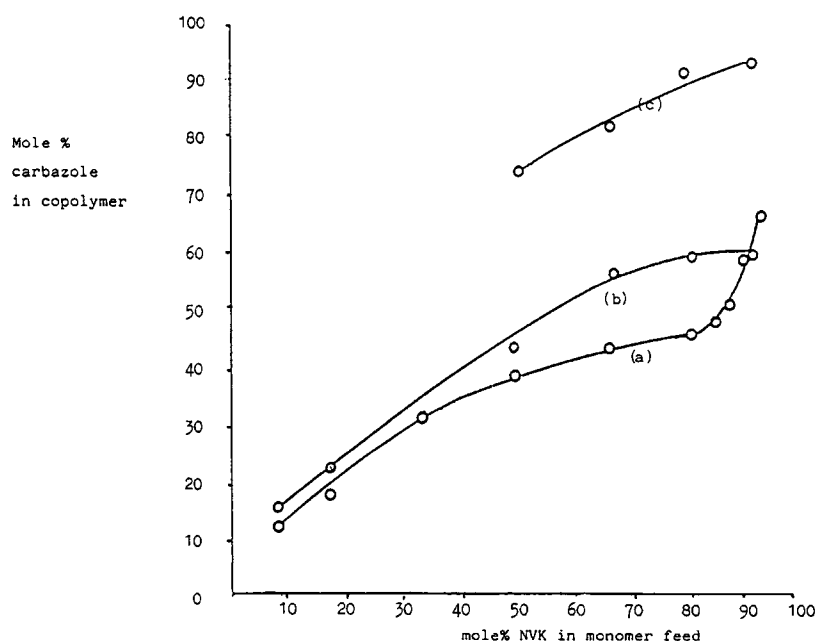**Table IV   Copolymers of *N*-Vinylcarbazole: % Yields and Molecular Weights (Daltons)**

	Molar Feed Ratio	1 : 10	1 : 5	1 : 2	1 : 1	2 : 1	4 : 1	10 : 1
Comonomer								
Acrylic acid	% yield	11	23	50	61	55	40	31
	M_w/D	1350	2500	7200	6380	9540	7900	9240
Methacrylic acid	% yield				71	65	50	36
	M_w/D				19400	19100	16500	12400
Fumaric acid	% yield				11	18	12	9
	M_w/D				1000	1370	1460	5240
Itaconic acid	% yield				62	53	40	32
	M_w/D				8100	7300	6660	5050
Maleic anhydride	% yield				9	15	13	18
	M_w/D				1510	1820	3230	5000
Itaconic anhydride	% yield				58	51	42	33
	M_w/D				1930	4420	6000	11000

suitable solvent (e.g., methyl ethyl ketone, MEK) and spin coated at 70 rpm onto an anodized aluminum sheet. The coated aluminum sheets were then baked for 5 min at 120°C. On cooling, each plate was placed in a tray containing Electrosol 85, a commercial decoating preparation consisting of an alkaline soap solution at pH 12. The tray was repeatedly tipped so that the solution washed across the plate surface, removing the copolymer layer. If any copolymer film remained after 1 min, the copolymer was judged to be insoluble.
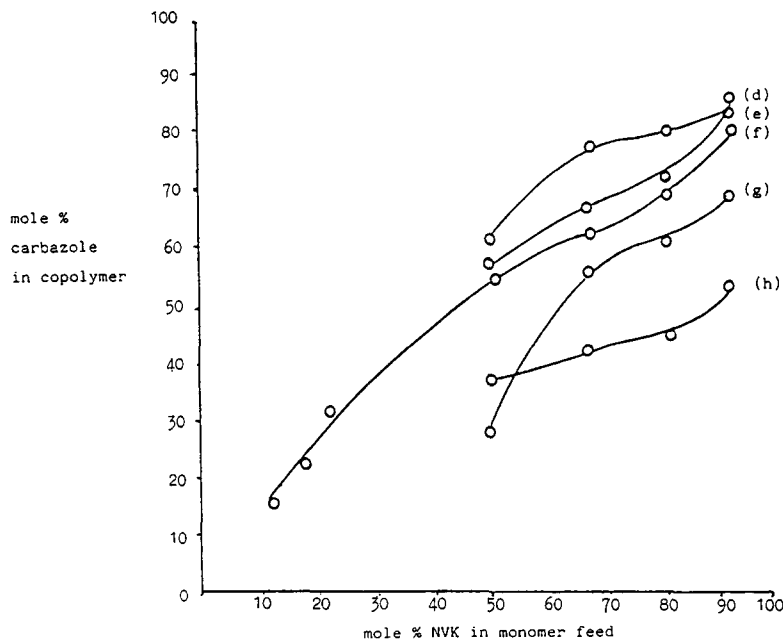
RESULTS

Table III shows those instances in which successful formation of copolymer took place for the different monomer pairs. It was noticed that only the strongly acidic comonomers gave appreciable yields of copolymer. Weakly acidic and/or sterically large comonomers gave poor yields.

Table IV gives the molar mass values for the copolymers. These average molar mass values are low

Figure 1   Variation of copolymer composition with monomer feed for copolymers of NVK with (a) acrylic acid, (b) methacrylic, and (c) crotonic acid.

Figure 2 Variation of copolymer composition with monomer feed for copolymers of NVK with (d) fumaric acid, (e) itaconic anhydride, (f) itaconic acid, (g) maleic anhydride, and (h) citraconic anhydride.

considering that the copolymers were synthesized in a nitrogen atmosphere. Steric exclusion chromatography shows that these molar mass values generally center around 2×10^4 daltons. These results are similar to those achieved by Shirota and Yoshimura for copolymers of NVK with fumarate esters, maleate esters, and maleic anhydride.[11,19-21] Some examples of copolymer yields and average molar mass values for the comonomer pairs are also given in Table IV.

Relationships between molar feed ratios and copolymer compositions are illustrated in Figures 1 and 2 for monobasic and dibasic comonomers, respectively. Generally, these resemble those for poly(NVK-co-acrylic acid) samples reported by Chapiro[12,13] and poly(NVK-co-acrylonitrile) reported by Tazuke.[22] For the more strongly acidic comonomers a plateau feature is seen in each curve beginning at approximately equimolar feed, thus indicating that the copolymer composition remains approximately constant with increasing concentrations of NVK monomer. As the yields of copolymer generally drop in this area (see Table IV), it must be assumed that copolymer composition is constant and that alternating copolymers are being produced. This has also been reported by Chapiro.[12,13]

The steep rises seen in Figures 1 and 2 at high NVK–monomer feeds are indicative of the formation of long chains of PVK in the copolymers.

Table V shows the reactivity ratios for the copolymerization of NVK with several comonomers. Reactivity ratios were calculated using the following form of the copolymerization equation:

$$\frac{f_1(1 - 2F_1)}{F_1(1 - f_1)} = \frac{r_1 f_1^2 (F_1 - 1)}{F_1(1 - f_1)^2} + r_2$$

where f_1 = mole fraction of NVK in monomer feed
F_1 = mole fraction of NVK in copolymer
r_1 = reactivity ratio of NVK
r_2 = reactivity ratio of comonomer

Copolymer Decoating

A major advantage was gained immediately by the use of copolymers of NVK rather than PVK ho-

Table V   Reactivity Ratios of Copolymers of *N*-Vinylcarbazole

Comonomer	r_1 (NVK)	r_2 (Comonomer)
Acrylic acid	0.58	0.57
Methacrylic acid	0.16	0.44
Crotonic acid	1.91	0.01
Itaconic acid	0.26	0.20
Itaconic anhydride	0.55	0.03
Maleic anhydride	0.12	0.12
Fumaric acid	0.23	0.07

Table VI   Decoating Speeds at pH 12 of NVK-Carboxylic Acid–Anhydride Copolymers

Comonomer	Ratio (NVK–Comonomer) Feed	Actual	Coating Solvent	Decoat Time (s)
Acrylic acid	1 : 1	0.92 : 1	Acetone	20
Acrylic acid	2 : 1	1.19 : 1	Acetone	25
Acrylic acid	4 : 1	1.27 : 1	Acetone	25
Acrylic acid	10 : 1	1.45 : 1	Acetone	60
Methacrylic acid	1 : 1	0.76 : 1	Tetrahydrofuran	30
Methacrylic acid	2 : 1	1.25 : 1	Tetrahydrofuran	50
Methacrylic acid	4 : 1	1.35 : 1	Tetrahydrofuran	60
Methacrylic acid	10 : 1	1.52 : 1	Tetrahydrofuran	60
Itaconic aicd	1 : 1	1.15 : 1	Ethanol	20
Itaconic acid	2 : 1	1.56 : 1	Tetrahydrofuran	23
Itaconic acid	4 : 1	1.98 : 1	Tetrahydrofuran	40
Itaconic acid	10 : 1	3.10 : 1	Tetrahydrofuran	60
Maleic anhydride	1 : 1	1.05 : 1	Methyl ethyl ketone	50
Maleic anhydride	2 : 1	1.15 : 1	Methyl ethyl ketone	60
Maleic anhydride	4 : 1	1.44 : 1	Methyl ethyl ketone	60
Maleic anhydride	10 : 1	1.19 : 1	Methyl ethyl ketone	60
Citraconic anhydride	1 : 1	0.57 : 1	Methyl ethyl ketone	60
Citraconic anhydride	2 : 1	0.69 : 1	Methyl ethyl ketone	60
Citraconic anhydride	4 : 1	0.75 : 1	Methyl ethyl ketone	60
Citraconic anhydride	10 : 1	0.59 : 1	Methyl ethyl ketone	60
Fumaric acid	1 : 1	1.19 : 1	Methyl ethyl ketone	20
Fumaric acid	2 : 1	1.45 : 1	Methyl ethyl ketone	25
Fumaric acid	10 : 1	5.80 : 1	THF	60

mopolymer in that most copolymers were soluble in solvents that are acceptable to the reprographics industry. The solvents include methyl ethyl ketone, acetone, and ethanol. Tetrahydrofuran and toluene, which are the usual solvents for PVK, are not suitable for use in the reprographics industry.

For all the copolymers tested, the film-forming properties were inferior to those of PVK itself, presumably due to the lower molar mass values of these copolymers. The alkali-decoating speeds of the copolymers were measured and the results are given in Table VI.

Table VI follows a fairly logical pattern, the decoating times becoming greater with decrease in the acid group concentration of the copolymer films.
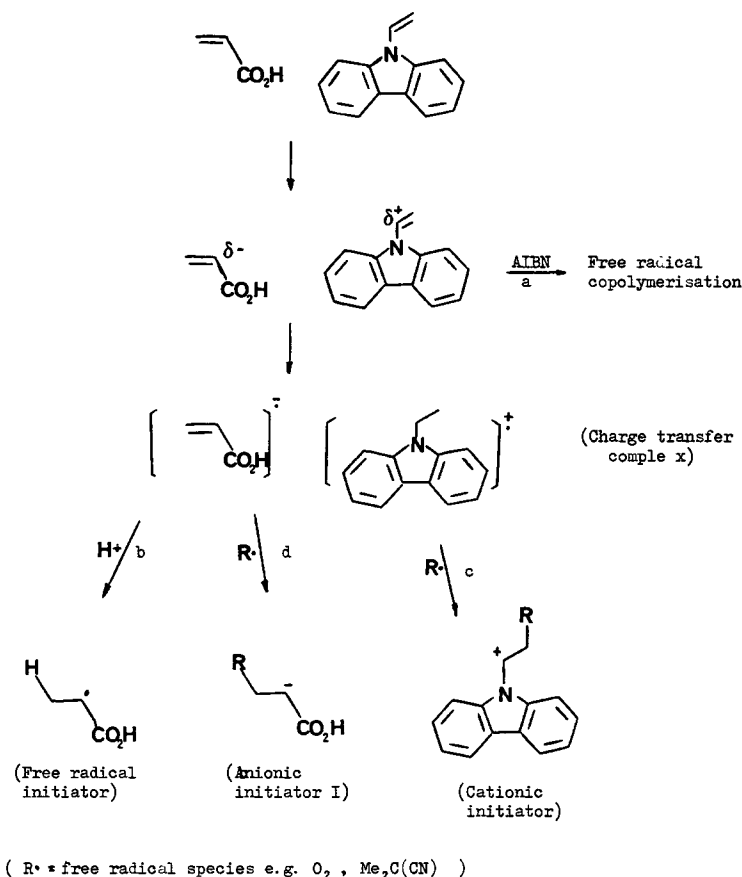
DISCUSSION

Copolymerization Mechanisms

Figures 1 and 2 show that the copolymer systems approximate to ideal compositional behavior if up to equimolar feeds are used. Here, however, the plots for those copolymers with the more strongly electron-accepting comonomers plateau out. Tazuke has suggested that weak charge transfer complexes are formed by NVK with electron acceptors such as acrylonitrile.[22] Monomers such as acrylic acid, fumaric acid, and itaconic acid would thus be expected to form similar complexes with NVK. It is clear that, in the region of equimolar feeds, charge transfer complex formation may be universal. These complexes may initiate cationic, anionic, and free-radical copolymerization as shown in Figure 3. In Figure 3 acrylic acid is shown as the representative comonomer.

Copolymers formed from approximately equimolar feeds of the two monomers were found (by fluorescence spectroscopy)[16] to be alternating in character. Also, on treatment of the copolymerizations with carbon tetrabromide, a free-radical inhibitor, the copolymers obtained were found to be of similar construction to those formed in uninhibited reactions. It is therefore inferred that at equimolar comonomer feeds the copolymerizations fol-

Figure 3   Initiation pathways involving charge transfer complexes of NVK with acrylic acid.

low either route (a) or (b) of Figure 3. The fact that no copolymerization or homopolymerization products resulted from reactions without azobis (isobutyronitrile) suggests that route (a) is the more likely.

Greater percentages of the carbazole unit were observed in the copolymers formed with electron acceptors at higher NVK feeds. Additionally the fluorescence spectra of these copolymers show greater PVK character.[16] Such behavior also occurred when free-radical inhibitors were used in the copolymerizations at high NVK feeds. The inference here is that, as the mole percentage of NVK in the monomer feed is increased above the equimolar point, the cationic route [(c), Fig. 3] is followed, the cationic species necessary possibly being provided by the reaction of the N-vinylcarbazole radical cation with decomposition products of AIBN. Such dual nature in NVK copolymerization has also been reported by Barrales-Rienda.[23]

The anionic route [(d), Fig. 3] might have been expected at high concentrations of acidic monomer, but this was never observed, presumably due to acidic quenching of the anion I.

Crotonic acid and methacrylic acid did not exhibit this behavior because they are much weaker electron acceptors. This is due to the presence of the olefinic methyl group. However, the anhydrides used in copolymerizations all gave strong charge transfer complexes with NVK. This was noticeable, in each case, as a strong yellow coloration of the reaction mixture. Nevertheless, the resulting copolymers did not show the expected large increases in PVK content at high NVK feed ratios. It is therefore suggested that the increases seen in the case of electron-accepting carboxylic acids were due in part to the interaction of the acidic protons in the copolymerization mechanism, perhaps increasing the rate of cationic homopolymerization of NVK. Acid-initiated homopolymerization of NVK was first reported by Hoegl[3] who polymerized NVK with trichloroacetic acid as catalyst.

Copolymer Film Decoating

The copolymers behaved generally as expected. Increasing the carboxylic acid functionality of the monomer feed gave copolymers that decoated more

rapidly. Also the more acidic the comonomer used in copolymerization the higher was the decoating speed. For example, poly(NVK-co-acrylic acid) with an NVK–acid ratio of 1.27 : 1 decoated completely in 25 s. For the much weaker methacrylic acid copolymer at a similar composition (1.25 : 1), the decoating time was 50 s. At pH 12 the copolymers derived from dicarboxylic acids were clearly quicker to decoat.

The maleic anhydride and citraconic anhydride copolymers gave poor performances in alkali decoating tests. Again, taking similar copolymeric ratios, poly(NVK-co-maleic anhydride) at a ratio of 1.15 : 1 took longer than one minute to be decoated. Poly(NVK-co-fumaric acid) at a ratio of 1.19 : 1 took only 20 s. The behavior of the maleic anhydride copolymers was as expected since commercial lithographic binding resins contain copolymerized maleic anhydride as its ring-opened half ester. The poor decoating properties of poly(NVK-co-maleic anhydride) samples can thus be related to the time taken to hydrolyze the cyclic anhydride moieties.

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