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Preparation of new copolymers of vinyl acetate and *N*-substituted maleimides

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Eighteen new copolymers were prepared by the free-radical copolymerization of vinyl acetate with various *N*-substituted maleimides. These copolymers showed lower softening points than the corresponding homopolymers of the *N*-substituted maleimides. The decreases in the softening points were proportional to the vinyl acetate contents of the prepared copolymers. However, their molecular weights were higher than those of the corresponding homopolymers. In addition the new copolymers were soluble in common solvents and formed thermoplastic films. The reactivity ratios of both of the comonomers were less than 1, thus indicating a high possibility of alternating copolymers being formed. Copyright © 1996 Elsevier Science Ltd

(Keywords: copolymerization; vinyl acetate; *N*-substituted maleimides)

INTRODUCTION

Many monomers that do not homopolymerize, or produce low-molecular-weight polymers, might undergo copolymerization reactions to yield good polymers, provided that the comonomers are properly selected. For example, maleic anhydride does not homopolymerize, but undergoes copolymerization with styrene and other suitable monomers to produce commercially useful materials[1,2]. *N*-substituted maleimides are known to homopolymerize both free-radically and anionically to give low-molecular-weight polymers[3,4]. This is in contrast to the behaviour of maleic anhydride itself. Both the latter and the maleimides are five-membered ring species with vinyl groups that are 1,2-disubstituted. The exact reason for the polymerization of *N*-substituted maleimides is not known [5].

In order to investigate the possibility of obtaining better polymers from the *N*-substituted maleimides, vinyl acetate was chosen as a suitable comonomer, since the latter is electron-rich while the maleimides are electron-deficient species. As such, the two comonomers might interact well enough to produce good copolymers[6]. A few reports of such studies can be found in the literature[7,8], but they are limited in scope.

This present report considers a large number of *N*-substituted maleimides and bismaleimides, and their reactions with vinyl acetate.

EXPERIMENTAL

Preparation of N-*substituted maleimides*

Standard literature procedures were followed for preparing the *N*-substituted maleimides[3,9]. The products were purified by recrystallization from hexane or other suitable solvents. *Table 1* contains details of the melting points, percentage yields and elemental analyses of the *N*-substituted maleimides prepared in this work.

Copolymerization of vinyl acetate with N-*substituted maleimides*

Equimolar amounts of *N*-substituted maleimide and vinyl acetate were dissolved in a certain amount of freshly distilled suitable solvent in a screw-capped polymerization vessel, and an amount of azoisobutyronitrile (AIBN) equivalent to 0.02 wt% of monomer was added. The container was purged with nitrogen gas for a few minutes and then firmly stoppered. The clear solution was maintained at 80–82°C in a constant-temperature water bath for 3 h, and then poured into a beaker containing 150 ml of methanol in order to precipitate the copolymer. The precipitate was filtered, washed several times with methanol or ethanol, and finally dried *in vacuo*.

When greater than equimolar equivalents of vinyl acetate were used in the reactions some poly(vinyl acetate) homopolymer was found adhering to the walls of the reaction flask. *Table 2* lists the physical properties of the poly[vinyl acetate-*co*-*N*-(substituted maleimide)]s prepared in this work, with their elemental analysis results being given in *Table 3*.

RESULTS AND DISCUSSION

The various *N*-substituted maleimides were allowed to copolymerize with vinyl acetate using AIBN as the initiator. Vinyl acetate was chosen as the comonomer based on the fact that its vinyl group is rich in electrons as a result of the attached acetoxy group. On the other hand, the maleimides vinyl groups are electron deficient since two carbonyl groups are attached to them.

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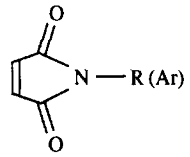
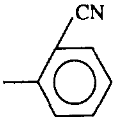
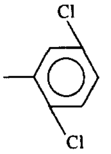
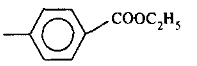
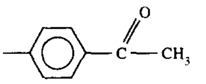
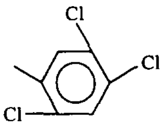
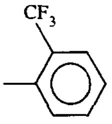
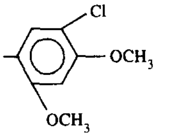
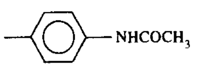
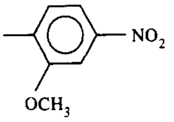
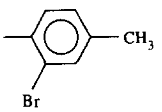
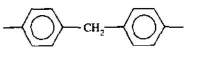
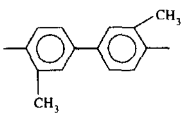
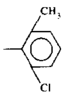
Table 1 Melting points, percentage yields, and elemental analysis results of the *N*-substituted maleimides prepared in this work



R(Ar)	M.p. (°C)	Yield (%)		Elemental analysis (%) C	H	N
	92	65	C[a]	66.66	3.03	14.14
			F[a]	66.50	3.20	14.03
	100	65	C	49.58	2.06	5.78
			F	49.50	2.12	5.65
	106	60	C	63.15	4.48	5.71
			F	63.40	4.60	5.55
	144	80	C	66.97	4.21	6.50
			F	67.00	4.40	6.
	107	68	C	43.39	1.44	5.06
			F	43.25	1.55	4.98
	111	50	C	55.46	2.52	5.88
			F	54.95	2.60	5.71
	175	50	C	53.83	3.73	5.23
			F	53.89	3.83	5.06
	210[b]	55	C	62.60	4.34	12.17
			F	62.50	4.42	12.25
	140	50	C	53.22	3.22	11.29
			F	53.08	3.34	11.09
	Oil	70	C	50.19	1.90	5.32
			F	50.30	2.01	5.40
	155	60	C	70.39	3.91	7.82
			F	70.60	4.05	7.45
	220	60	C	70.96	4.30	7.52
			F	70.56	4.55	7.60
	78	75		–	–	–

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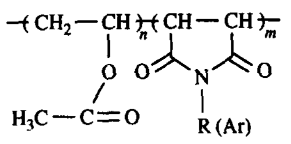
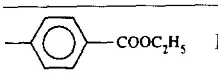
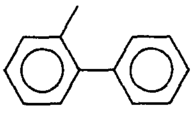
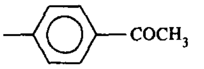
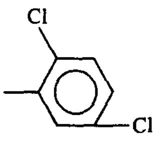
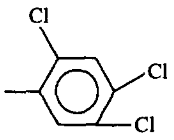
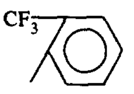
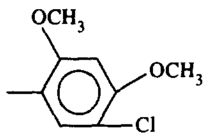
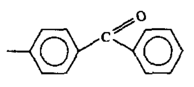
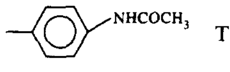
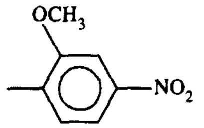
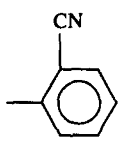
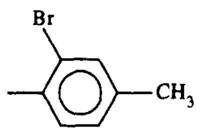
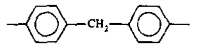
[a] C, calculated; F, found

[b] Decomposes

Table 2 Physical properties of the prepared poly [vinyl acetate-*co*-*N*-(substituted maleimides)]

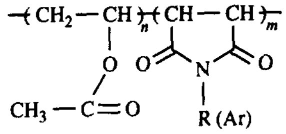


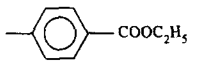
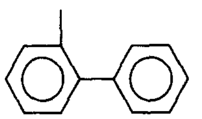
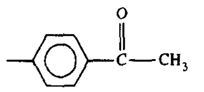
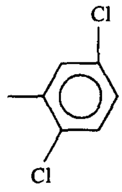
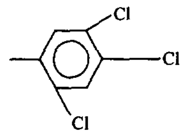
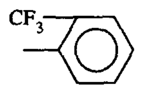
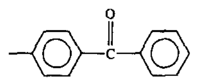
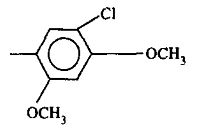
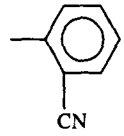
R (Ar)	Solvent	Softening point[a] (°C)	Conversion (%)	$[\eta]^b$ (dl/g)
	Benzene	205–215	90	0.539
	Benzene	220–230	90	0.473
	Benzene	230–240	80	0.529
	Benzene	255–265	85	0.657
	Benzene	230–240	80	0.412
	Benzene	255–270	90	0.420
	THF	235–245	85	0.459
	Benzene	205–215	85	0.540
	THF	225–245	80	0.507
	Benzene	215–230	40	0.499
	Benzene	240–250	80	0.364
	Benzene	233–245	85	0.443
	Benzene	360	90	–

[a] Determined by using a Vicat or hot-stage apparatus

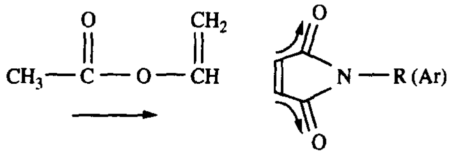
[b] Determined by using an Ubbelohde-type automatic viscometer

Table 3 Elemental analysis results obtained for some of the copolymers prepared in this study



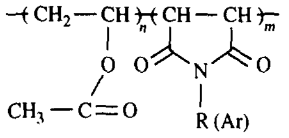
R (Ar)		Elemental analysis (%) C	H	N
	C[a] F[a]	61.63 61.04	5.13 5.10	4.22 5.08
	C F	71.64 73.44	5.07 5.50	4.17 4.94
	C F	63.78 62.43	4.98 4.95	4.65 5.43
	C F	51.21 53.42	3.35 3.67	4.26 5.16
	C F	46.34 46.77	2.75 2.70	3.86 4.48
	C F	55.55 57.28	3.70 4.14	4.32 3.90
	C F	69.42 69.29	4.68 3.92	3.85 4.76
	C F	54.31 54.20	4.52 4.25	3.96 3.98
	C F	63.38 62.32	4.22 3.74	9.85 9.45

[a] C, calculated; F, found



Comonomer systems such as the above are likely to produce high-molecular-weight alternating copolymers[10]. Benzene, tetrahydrofuran (THF), or dioxane were used as solvents for the copolymerization reactions. The new copolymers had higher molecular weights than the corresponding homopolymaleimides[3,4] but their thermal stabilities were reduced.

Table 4 N.m.r. spectroscopic data obtained for some of the copolymers prepared in this study



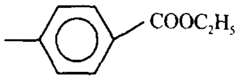
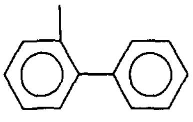
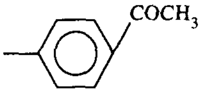
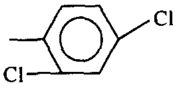
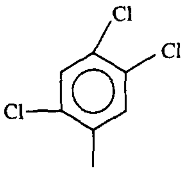
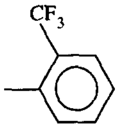
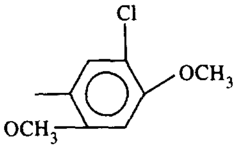
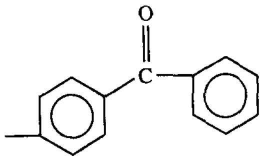
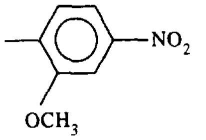
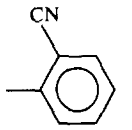
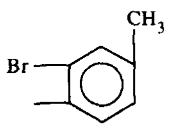
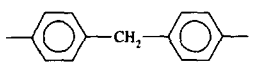
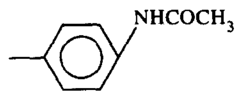
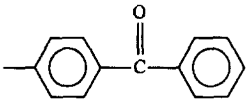
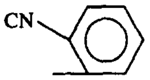
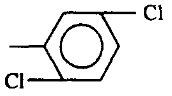
R (Ar)	Chemical shift, δ (ppm)
	5.60 (s,2H, -CH-CH-, maleimide); 7.50–8.00 (sb, aromatic); 3.40 (s, 2H-CH$_2$-); 1.91 (sb, 1H, -CHO); 1.31 (t, 3H, -COCH$_3$)
	1.80 (s, 3H, -COCH$_3$); 2.01 (t, 1H, -CHO); 3.22 (t, 2H, -CH$_2$); 5.21 (sb, 2H, -CH-CH-, maleimide); 7.30 (sb, 9H, aromatic)
	1.81 (s, 3H, -COCH$_3$); 2.30 (t, 1H, -CHO), 3.2 (t, 2H, -CH$_2$-); 5.50 (sb, 2H, -CH-CH-, maleimide); 7.31 (sb, 4H, aromatic)
	1.31 (s, 3H, -COCH$_3$); 1.90 (t, 1H, -CHO); 3.11 (t, 2H, -CH$_2$-); 5.40 (sb, 2H, -CH-CH-, maleimide); 7.41 (sb, 3H, aromatic)
	1.40 (s, 3H, -COCH$_3$); 2.04 (t, 1H, -CHO-); 3.11 (sb, 2H, -CH$_2$-); 5.60 (sb, 2H, -CH-CH-, maleimide); 7.80, 8.11 (s, 1H, aromatic)
	1.51 (s, 3H, -COCH$_3$); 2.20 (t, 1H, -CHO); 3.20 (sb, 2H, -CH$_2$-); 5.71 (sb, 2H, -CH-CH-, maleimide); 7.90 (m, 4H, aromatic)
	2.00 (s, 3H, -COCH$_3$); 2.02 (t, 1H, -CHO); 3.31 (sb, 2H, -CH-); 3.80, 3.90 (s, 3H two-OCH$_3$); 5.60 (sb, 2H, -CH-CH-, maleimide); 6.91 (s, 2H, aromatic)
	1.81 (s, 3H, -COCH$_3$); 1.90 (t, 1H, -CHO); 3.02 (sb, 2H, -CH$_2$-); 5.60 (sb, 2H, -CH-CH-, maleimide); 7.50 (m, 9H, aromatic)
	1.51 (s, 3H, -COCH$_3$); 1.91 (sb, 1H, -CHO); 3.11(t, 2H, -CH$_2$-); 3.90 (s, 3H, -OCH$_3$); 5.60 (sb, 2H, -CH-CH-, maleimide); 7.60, 8.11 (s, m, 3H, aromatic)
	2.00 (s, 3H, -COCH$_3$); 2.04 (t, 1H, -CHO); 3.11 (b, 2H, -CH$_2$-); 5.70 (sb, 2H, -CH-CH-, maleimide); 7.50, 8.00 (d, s, 4H, aromatic)
	1.50 (t, 3H, -COCH$_3$); 1.52 (t, 1H, -CHO); 2.10 (s, 3H, -CH$_3$); 3.21 (b, 2H, -CH$_2$-); 5.51 (sb, -CH-CH-, maleimide); 7.30, 7.62 (d, s, 3H, aromatic)
	1.40 (s, 3H, -COCH$_3$); 2.00 (s, 1H, -CHO); 2.90 (t, 3H, -CH$_2$-); 3.71 (s, 2H, CH$_2$ between phenyls); 4.42 (s, 2H, -CH-CH-, maleimide); 7.41 (m, 8H, aromatic)
	1.80 (s, 3H, -COCH$_3$); 1.80 (sb, 1H, -CHO); 3.11 (t, 2H, -CH$_2$-); 5.42 (sb, 2H, -CH-CH-, maleimide); 7.00, 7.50, 7.61 (all s, 4H, aromatic); 9, 90 (sb, 1H, -NH-CO)

Table 5 Reactivity ratios of selected *N*-substituted maleimides in their copolymerization reactions with vinyl acetate[a]

Substitutent	r_1	r_2
	0.28	0.07
	0.22	0.07
	0.36	0.35

[a] r_1 and r_2 represent reactivities of maleimide and vinyl acetate, respectively

Compared to the corresponding homopolymers, the new copolymers showed lower softening points and better solubilities in organic solvents, with the exception of poly[vinyl acetate-*co*-bis-*N*,*N*(*p*,*p*-phenylmethyl)-maleimide] which softened at 360°C and did not dissolve in any of the solvents, including dimethyl formamide (DMF). An increase in the molar ratio of the maleimide relative to the vinyl acetate in these experiments resulted in the formation of copolymers with higher softening points. On the other hand, increases in the amount of vinyl acetate lowered the softening points of the resulting copolymers. This result was expected since incorporation of vinyl acetate into the repeat units would facilitate free rotations around the methylene bond, plus the fact that the vinyl acetate segments are less bulky and of low polarity. All of these factors would affect the glass transition points (T_gs), softening points, and solubilities of the new copolymers. However, in general the copolymers obtained had alternating-type structures, regardless of the stoichiometry of the reactants.

The structures of the copolymers were confirmed by infra-red (i.r.) and nuclear magnetic resonance (n.m.r.) spectroscopy, and elemental analysis. Results obtained from the latter corresponded to the alternating copolymer type in most cases. This was also evident from their i.r. and n.m.r. spectra. *Table 3* contains the results from elemental analysis, while *Table 4* lists the n.m.r. spectral data of the prepared copolymers. The i.r. spectra of the various copolymers were all similar, showing major absorptions at 1700–1720 cm^{-1} (C = O, maleimide) and 1740–1770 cm^{-1} (C = O, ester), in addition to C–N absorptions at around 1380–1390 cm^{-1}.

The reactivity ratios of the comonomers were determined by using the following method. Three different concentrations of the comonomers were used in the copolymerization experiments, with the initial solutions of the maleimides having the following concentrations: 80, 50, and 20 mol%. After adding the corresponding amounts of vinyl acetate, AIBN and solvent, the polymerizations were carried out as previously described. The polymerization process was interrupted early, and the unreacted *N*-substituted maleimide was isolated from the filtrate after precipitation and removal of the copolymer. In these experiments, all of the vinyl acetate was incorporated into the copolymer when the maleimides were used in excess, with the copolymer obtained being of the alternating type. Determination of the reactivity ratios was achieved by using the Mayo–Lewis equation[11] (*Table 5*).

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