4814 *Macromolecules* **1993**, *26*, 4814-4817

Water-Soluble Copolymers. 47. Copolymerization of Maleic Anhydride and *N*-Vinylformamide

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Received March 16, 1993; Revised Manuscript Received May 21, 1993

ABSTRACT: The free-radical copolymerization of maleic anhydride (MA) and *N*-vinylformamide (NVF) in homogeneous solution has been studied in the range from 10 to 90 mol % NVF in the feed. The copolymer compositions have been determined from elemental analysis and ^{13}C NMR. Reactivity ratios were calculated by Fineman-Ross, Kelen-Tudos, and nonlinear least-squares methods and indicate that the monomer pair has a strong tendency to alternate. MA and NVF were found to form a charge-transfer complex in both chloroform and THF. The equilibrium constant and composition of the charge-transfer complex were calculated from the modified Benesi-Hildebrand equation.

Introduction

Maleic anhydride (MA) does not homopolymerize by normal free-radical polymerization but can readily form alternating copolymers with electron-donor monomers such as styrene,[1] vinyl ethers,[2] and vinyl acetate.[3] *N*-Vinylformamide (NVF), on the other hand, can homopolymerize and copolymerize to high molecular weight.[4,5] Here we report the synthesis and characterization of the copolymers derived from MA and NVF. The possibility of complexation of MA and NVF has also been investigated.

Experimental Section

Materials. Maleic anhydride was recrystallized from chloroform and vacuum dried at room temperature (mp 55-55.5 °C). *N*-Vinylformamide, supplied by Air Products Inc., was distilled twice under reduced pressure prior to use (bp 60-61 °C at 0.5 mmHg). AIBN was recrystallized from ethanol. THF and chloroform were spectroscopic grade and used as received.

Measurements. Infrared spectra were obtained from a Mattson Model 2020 FTIR. ^{1}H and decoupled ^{13}C NMR spectra of the copolymer samples were recorded on Bruker 200-MHz and 300-MHz instruments, using DMSO-d_6 as solvent. Classical light scattering studies were performed with a Chromatix KMX-6 low-angle laser light scattering spectrophotometer with a 2-mW He-Ne laser operating at 633 nm. Refractive index increments (d*n*/d*c*) were obtained using a Chromatix KMX-16 differential refractometer. NVF purity was determined with a Hewlett-Packard 5890 Series II GC instrument. The UV absorption of all samples was measured with a Hewlett-Packard 8452A UV/vis spectrophotometer at room temperature. Elemental analyses were conducted by M-H-W Laboratories of Phoenix, AZ.

Copolymerization. MA and NVF were copolymerized by free-radical polymerization in THF under nitrogen at 65-67 °C using 0.1 mol % AIBN as the initiator. The feed ratio of NVF/MA was varied from 10/90 to 90/10 (Table I).

In a typical synthesis involving 60 mol % NVF in the feed, MA (8.06 g, 0.0822 mol), NVF (8.90 g, 0.125 mol), AIBN (0.0340 g, 2.07×10^{-4} mol), and THF (100 mL) were placed in a 250-mL flask equipped with a magnetic stirrer, a nitrogen inlet, and a condenser. The mixture was purged with prepurified nitrogen for 30 min and then immersed in an oil bath at 65 °C. Copolymerization was allowed to proceed to about 10% conversion. The copolymer was then precipitated in ether, filtered, purified by successive precipitations in ether from DMF, and then dried under vacuum at room temperature for 24 h.

Determination of Charge-Transfer Complex Formation between MA and NVF. The stock solutions of MA in two different solvents, chloroform and THF, were prepared in 500-mL volumetric flasks. The solutions of MA and NVF were obtained by adding an appropriate amount of NVF to 20 mL of a MA stock solution. The initial concentrations of MA and NVF in such solutions ranged in chloroform from 0.00427 to 0.00483 M and from 0.492 to 2.14 M, respectively (Table III), and in THF from 0.00438 to 0.00482 M and from 0.508 to 1.760 M (Table IV).

Results and Discussion

Monomer Purification and Copolymerization. NVF, as supplied, contains 4% formamide and other impurities. Initial attempts at purification of NVF, involving successive extraction of formamide with a small amount of water from a benzene solution, let to a 98.8% pure product. However, the yield from this method was only about 10%. Multiple vacuum distillations proved to be more efficient. The purity of NVF was 98.2% after two distillations with 78% recovery.

Copolymerizations of MA and NVF were carried out in four organic solvents: benzene, DMF, THF, and ethyl acetate. Copolymerization in benzene yielded a light-orange precipitate which gradually became tacky in the air and was difficult to purify. The product obtained in DMF was precipitated into ether as a light-brown solid. MA and NVF copolymerized most effectively in THF and ethyl acetate. The polymers precipitated as white or slightly yellow solids. Dissolution in DMF and reprecipitation from ether yielded white substances.

Copolymer Composition and Reactivity Ratios. Distinct carbonyl resonances from MA and NVF occur at 173-175 and 160-165 ppm, respectively, in ^{13}C NMR spectra and are useful for the estimation of copolymer composition. The mole fraction of each monomer in the respective copolymers was obtained by integration of the ^{13}C carbonyl resonances of MA and NVF as shown in Table I. Compositional information from NMR agreed favorably with that obtained from elemental analysis utilizing the equation

$$wt\ \%\ N = \frac{14.01 m_1}{71.02 m_1 + 98.06\,(1 - m_1)} \times 100$$

where wt % N represents the weight percentage of nitrogen in the copolymers and m_1 is the mole fraction of NVF units.

The reactivity ratios from NVF (M_1) and MA (M_2) were calculated by the graphical methods of Fineman-Ross[6] and Kelen-Tudos[7] and by a nonlinear least-squares method.[8] The results are summarized in Table II.

0024-9297/93/2226-4814$04.00/0

Table I. Copolymerization of NVF and MA

NVF_1[a] (M_1) (mol %)	NVF_E[b] (M_1) (mole %)	$[NVF]_E$[c] (M)	[CTC] (M)	t (min)	convn (mol %)	NVF_c[d] (m_1) (mol %)	$M_w \times 10^{-4}$
10.1	6.60	0.0751	0.055	240	3.0	46.9	
20.6	15.6	0.169	0.10	480	10.3	47.7	
30.6	25.7	0.293	0.16	420	9.7	49.4	
40.4	37.7	0.460	0.24	210	8.8	50.3	
50.2	52.4	0.675	0.32	110	7.8	50.6, 51.8[e]	
60.4	65.0	0.932	0.32	70	9.0	52.3	8.5
70.1	77.2	1.15	0.27	30	9.8	53.8	
80.0	88.0	1.76	0.28	20	6.7	57.6, 55.9[e]	8.0
89.9	97.0	2.24	0.31	15	6.0	63.3	

[a] Initial mole fraction of NVF in the feed. [b] Mole fraction of NVF at equilibrium. [c] Equilibrium concentration of NVF. [d] Mole fraction of NVF in the copolymers. [e] From elemental analyses.

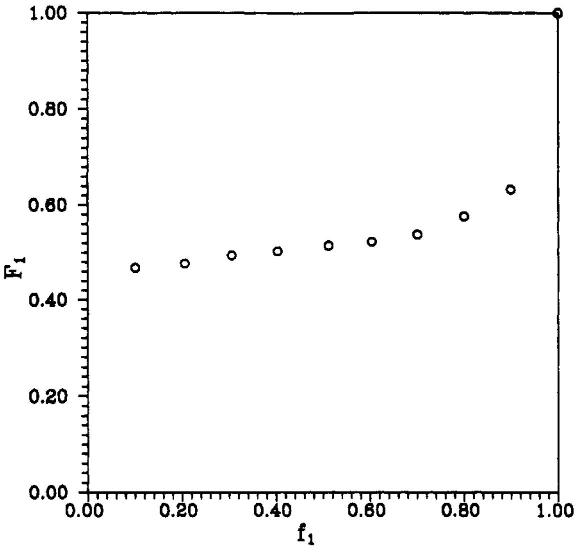

Figure 1. Mole percent of NVF in the NVF/MA copolymer as a function of the comonomer feed ratio.

Table II. Reactivity Ratios of NVF and MA

	r_1	r_2	r_1r_2
F–R	$(2.2 \pm 0.002) \times 10^{-2}$	-0.16 ± 0.01	
K–T	$(4.1 \pm 0.003) \times 10^{-2}$	$(1.1 \pm 0.001) \times 10^{-2}$	4.5×10^{-4}
NLS	$(2.8 \pm 0.026) \times 10^{-2}$	$(1.0 \pm 0.025) \times 10^{-2}$	2.8×10^{-4}

Table III. NVF/MA System in Chloroform at λ = 340 nm

$C_{MA} \times 10^2$ (M)	C_{NVF} (M)	A_{MA}	A_{NVF}	A_T	A^*
0.483	0.492	0.0182	0.0580	0.100	0.023
0.479	0.713	0.0180	0.0847	0.133	0.030
0.472	0.850	0.0178	0.1010	0.153	0.034
0.463	1.12	0.0174	0.136	0.193	0.040
0.454	1.36	0.0171	0.169	0.228	0.042
0.447	1.57	0.0168	0.192	0.256	0.047
0.440	1.75	0.0165	0.218	0.284	0.050
0.427	2.14	0.0160	0.259	0.333	0.058

To ascertain copolymer copolymerization behavior, the mole fraction of NVF in the copolymers was plotted as a function of the mole fraction of NVF in the feed. The curve in Figure 1 illustrates that the copolymers contain equimolar ratios of the monomers over a wide range of the composition of the feed, which suggests the formation of alternating structure. The alternating tendency of the comonomer pair is also indicated by their r_1r_2 product which approaches zero.

Studies of the Charge-Transfer Complex between MA and NVF. Several monomers that copolymerize with MA in an alternating manner through a free-radical mechanism form charge-transfer complexes. A charge-transfer complex might be expected to exist in the MA/NVF system. For MA and NVF to form a charge transfer complex (CTC), an equilibrium would exist

$$MA + n NVF \rightleftharpoons CTC \qquad (1)$$

for which the equilibrium constant is defined as

$$K = [CTC]/([MA][NVF]^n) \qquad (2)$$

where [CTC], [MA], and [NVF] are the concentrations of CTC, MA, and NVF, respectively. The degree of association of the complex is n. Values for K and n can be determined via a modified Benesi–Hildebrand technique. In the classical Benesi–Hildebrand method,[9] the absorbance of the complex at a given wavelength can be determined by the Beer–Lambert equation, provided the electron-donor monomer (D), the electron-acceptor monomer (A), and the solvent do not absorb at this wavelength

$$A_{CTC,\lambda} = \epsilon_{CTC,\lambda} L [CTC] \qquad (3)$$

$\epsilon_{CTC,\lambda}$ is the molar absorptivity of the CTC, and L is the path length of the sample.

If the donor molecules are in large excess,

$$[D] \gg [A], \text{ i.e., } [D] \approx [D]_0 \qquad (4)$$

the following relationship can be written:

$$L[A]_0/A_{CTC,\lambda} = 1/\epsilon_{CTC,\lambda} + (1/\epsilon_{CTC,\lambda})(1/K_0)(1/[D]_0{}^n) \qquad (5)$$

where $[A]_0$ is the initial concentration of the acceptor and K_0 is the equilibrium constant between the monomer pair and the charge-transfer complex. By choosing a proper n value, a plot of $L[A]_0/A_{CTC,\lambda}$ against $1/[D]_0{}^n$ should yield a straight line. $\epsilon_{CTC,\lambda}$ and K can be calculated from the slope and intercept, respectively.

When there is competition between the solvent and the electron-donor monomer for the acceptor sites, experimental approaches become more difficult and a more complicated mathematical equation[10] has to be solved to obtain n and K values. Examination of the recent literature provides no information about possible charge-transfer complex formation between MA and THF. However, Caze and Loucheux have shown that MA does not form a complex in chloroform.[10] We have studied the absorption of the MA/NVF systems in both chloroform and THF.

The absorption of MA/NVF in chloroform was measured at 340 nm. For this wavelength, there are weak absorptions of MA and NVF at the concentration studied (Table III), so the classical Benesi–Hildebrand method is not applicable in this case. Careful studies indicate that the absorptions of all components in solution obey the Beer–Lambert relationship under the experimental conditions. The total absorbance $A_{T,\lambda}$ is

$$A_{T,\lambda} = \epsilon_{CTC,\lambda} L [CTC] + \epsilon_{MA,\lambda} L [MA] + \epsilon_{NVF,\lambda} L [NVF] \qquad (6)$$

Noticing that

$$[MA] = [MA]_0 - [CTC] \qquad (7)$$

Table IV. NVF/MA System in THF

$C_{MA} \times 10^2$ (M)	C_{NVF} (M)	A_{MA} for 340/360 nm	A_{NVF} for 340/360 nm	A_T for 340/360 nm	A^* for 340/360 nm
0.482	0.508	0.0178/0	0.06055/0.00555	0.3411/0.1250	0.2578/0.1195
0.470	0.855	0.0173/0	0.09420/0.00883	0.4882/0.1802	0.3767/0.1714
0.461	1.120	0.0170/0	0.1220/0.01141	0.5580/0.1995	0.4190/0.1881
0.452	1.363	0.0165/0	0.1479/0.01433	0.6269/0.2297	0.4625/0.2154
0.438	1.762	0.0161/0	0.1889/0.01789	0.7326/0.2520	0.5271/0.2341

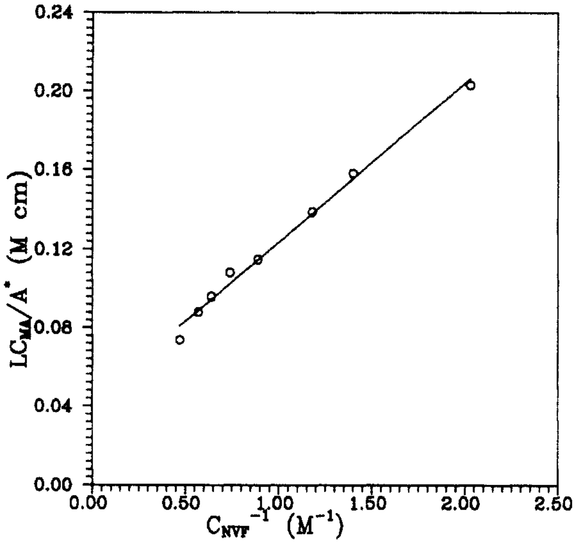

Figure 2. Modified Benesi–Hildebrand plot of LC_{MA}/A^* vs $1/C_{NVF}^{-1}$ for the NVF/MA solution in chloroform (λ = 340 nm).

and

$$[NVF]_0 \gg [MA]_0, \text{ i.e., } [NVF] \approx [NVF]_0 \qquad (8)$$

the Benesi–Hildebrand method may be applied using (1), (2), and (6)–(8)

$$L[MA]_0/A^* = 1/\epsilon^* + (1/\epsilon^*)(1/K)(1/[NVF]_0^{\,n}) \qquad (9)$$

where $[MA]_0$ and $[NVF]_0$ are the initial molar concentrations of MA and NVF, respectively, and

$$A^* = A_{T,\lambda} - \epsilon_{MA,\lambda}L[MA]_0 - \epsilon_{NVF,\lambda}L[NVF]_0$$

$$\epsilon^* = \epsilon_{CTC,\lambda} - \epsilon_{MA,\lambda}$$

A plot of $L[MA]_0/A^*$ vs $1/[NVF]_0$ yields a straight line (Figure 2), and the n, K, and $\epsilon_{CTC,\lambda=340\text{ nm}}$ values are summarized in Table V.

MA in THF exhibits almost the same molar absorptivity as in chloroform, indicating no complex formation between MA and THF. The n and K values of the MA/NVF system in THF were determined at wavelengths of 340 and 360 nm in a similar manner. The experimental data are summarized in Table IV and plotted in Figures 3 and 4. $\epsilon_{CTC,\lambda}$, n, and K are listed in Table V. The composition of the charge-transfer complex of MA and NVF is 1:1, as indicated by the n values of one in both THF and chloroform.

Copolymerization Mechanism. Molar concentrations of the charge-transfer complex in the copolymerization systems are calculated based on the equilibrium constant and listed in Table I. The copolymerization rate is not proportional to the concentration of the charge-transfer complex. Rather, the copolymerization rate increases with increasing NVF concentration. The above suggests that the alternating copolymerization results from the cross-addition of MA and NVF monomers to the propagating chain rather than the homopolymerization of the charge-transfer complex and that reaction of the maleic anhydride radical with the NVF monomer is the rate-determining step.

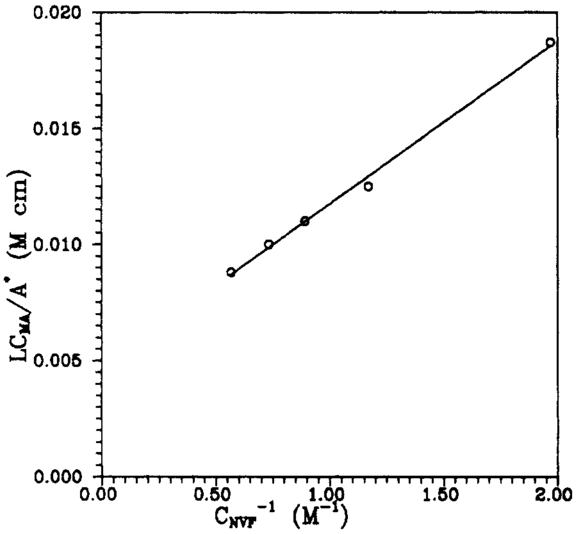

Figure 3. Modified Benesi–Hildebrand plot of LC_{MA}/A^* vs $1/C_{NVF}^{-1}$ for the NVF/MA solution in THF (λ = 340 nm).

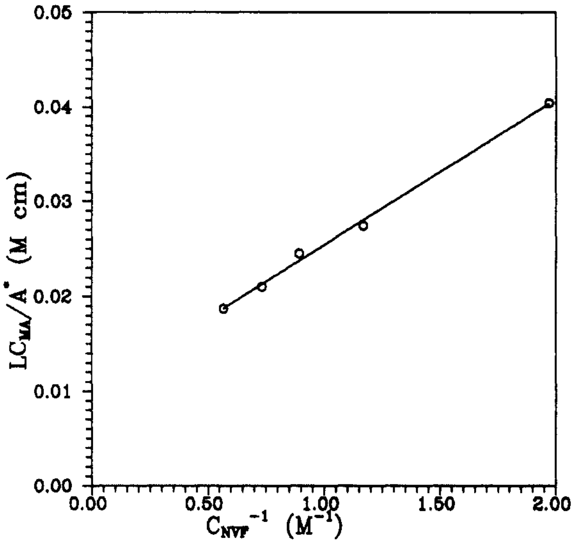

Figure 4. Modified Benesi–Hildebrand plot of LC_{MA}/A^* vs $1/C_{NVF}^{-1}$ for the NVF/MA solution in THF (λ = 360 nm).

Table V. K and $\epsilon_{CTC,\lambda}$ of the NVF/MA System in Chloroform and THF

solvent	λ (nm)	$\epsilon_{CTC,\lambda}$ (cm^{-1} M^{-1})	n	K (M^{-1})
$CHCl_3$	340	27	1	0.533
THF	340	214	1	0.680
THF	360	99	1	0.672

Conclusions

MA and NVF form a 1:1 charge-transfer complex in both chloroform and THF. Copolymerization of MA and NVF was performed in THF using AIBN as the initiator. The copolymer composition was determined by integration of ^{13}C carbonyl resonances of the monomer units. The reactivity ratios were calculated by three different methods, and these values indicate that the monomer pair has a strong tendency to form an alternating copolymer. The involvement of the charge-transfer complex in the alternating copolymerization is excluded since no direct relationship between the copolymerization rate and the concentration of the complex has been found. However, the data are not sufficient to ascertain at this point whether the complex is involved in the copolymerization.

Acknowledgment. The support of portions of this research by the Office of Naval Research, DARPA, and Air Products is gratefully acknowledged.

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