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CONTROLLED ACTIVITY POLYMERS. IV. COPOLYMERS OF 2-(1-NAPHTHYLACETYL)ETHYL ACRYLATE WITH HYDROPHILIC COMONOMERS: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

2-(1-Naphthylacetyl)ethyl acrylate (NAEA) was synthesized by esterification of 1-naphthylacetic acid (NAA) and 2-hydroxyethyl acrylate (HEA) and then polymerized to obtain the polymer-bound auxin NAA. The resulting polymer is potentially useful as a plant growth regulator through hydrolytic release of NAA. Copolymers of NAEA with hydrophilic comonomers were prepared by solution polymerization. The copolymer compositions were determined from elemental analysis, ^{13}C-NMR, and UV spectroscopy. The copolymer microstructure was predicted from the reactivity ratios in order to investigate the influence on the behavior of controlled release. These model structures will be utilized for assessment of structure/hydrolysis relationships in a subsequent paper.

INTRODUCTION

Controlled activity or controlled release from polymeric systems is becoming increasingly important in a variety of pharmaceutical, medical, and agricultural applications. The macromolecular nature of the delivery system allows

for control of mobility and period of effectiveness for the biologically active component.

Effective and economic methods of delivery are especially important for agents with high activity [1]. For such methods, controlled release technology holds great promise for improving the efficacy of existing drugs and pesticides and for reducing the problems associated with others. One approach is the preparation of polymerizable pesticide monomers and subsequent polymerization, alone or with a comonomer, to form a polymeric system for controlled hydrolytic release [2]. Release rates can be modified by changing the nature of the labile bond, its distance from the main polymer chain, and/or the polymer hydrophilicity.

In our initial work we reported a series of polymers with metribuzin, an amine-functional herbicide, pendently attached to poly(vinyl alcohol) through diisocyanate bridging groups and attached directly to cellulose, chitin, starch, and PVA [3-8]. These systems were effective in greenhouse studies at low rates of application. Continued work with metribuzin-containing polymers employed metribuzin-containing monomers to avoid problems inherent in performing reactions on polymers. Copolymerization of monomers having attached metribuzin with hydrophilic comonomers was investigated. Our group [9-11] has previously reported the synthesis and characterization of a number of polymers from herbicidal monomers.

In this paper we report the synthesis and characterization of the monomer 2-(1-naphthylacetyl)ether acrylate (NAEA), which contains the auxin 1-naphthylacetic acid (NAA), and its copolymers with hydrophilic comonomers. Auxins are a class of plant growth regulators which control the type of enzyme produced in the cell. The reasons for choosing plant-growth regulators as bioactive agents to be attached to the polymer chain are their potential for high efficacy at low concentration and their ecological acceptability [12]. Additionally, auxins possess strong ultraviolet chromophores and fluorescent properties which are especially useful for microanalysis.

EXPERIMENTAL

Materials

1-Naphthylacetic acid (NAA) from Sigma Chemical Co. was recrystallized from deionized water to give a melting point of 135-136°C. Acrylamide (AM) from Aldrich Chemical Co. was recrystallized twice from acetone and vacuum dried at room temperature (mp 83-84°C). The other liquid monomers were distilled in vacuum with hydroquinone prior to use: 2-hydroxyethyl acrylate

(HEA) at 0.25 torr, bp 43°C; 2-hydroxyethyl methacrylate (HEMA) at 0.75 torr, bp 67°C; methacrylic acid (MAA) at 2.5 torr, bp 46°C; acrylic acid (AA) at 4 torr, bp 37°C; *N*-vinyl-2-pyrrolidone (VP) at 0.25 torr, bp 43°C.

Azobisisobutyronitrile (AIBN) was recrystallized twice from ethyl alcohol. Potassium persulfate from J. T. Baker Co. was recrystallized twice from deionized water prior to use. Solvents used in polymerization and characterization were purified by distillation. All other chemicals were reagent grade and were used without further purification.

Monomer Synthesis

NAEA was prepared by esterification of NAA with HEA. To a stirred solution of 95.2 mmol NAA in 400 mL anhydrous diethyl ether were added 8 mmol 4-pyrrolidinopyridine (PPY) and 100 mmol HEA. Dicyclohexylcarbodiimide (DCC, 100 mmol) was added to the reaction mixture which was then stirred for 24 h at room temperature.

The synthesis of NAEA followed the procedure known as the PPY-catalyzed DCC method [13, 14]. *N,N*-Dicyclohexyl urea was filtered, and the filtrate was washed with water (1 X 300 mL), 5% acetic acid solution (3 X 300 mL), 5% sodium bicarbonate solution (3 X 300 mL), and water (1 X 300 mL). After drying over $MgSO_4$, the solution was filtered on a short silica column to remove particulates, and then solvent was removed by evaporation to give the ester. Upon drying under vacuum, a pale yellow liquid was obtained in 95% yield.

Analysis. Calculated for $C_{17}H_{16}O_4$: C, 71.84; H, 5.63. Found: C, 71.80; H, 5.94. IR (neat): aliphatic C–H, 2940; ester C=O, 1730; CH_2=CH, 1633, 1617; aromatic (naphthyl) C=C, 1590, 1510 cm^{-1}. λ_{max} 283.5 nm, ϵ_{max} 6710. ^{1}H NMR (DMSO-d_6, Fig. 1) δ4.14 (s, 2H, $-CH_2-$naphthyl), 4.30 (s, 4H, $-OCH_2CH_2O-$), 5.80-6.30 (m, 3H, CH_2=CH–), 7.20-8.10 ppm (m, 7H, naphthyl group protons). ^{13}C-NMR spectrum (neat, Fig. 2): δ39.5 (s, –CH–$\underline{C}H_2$–naphthyl), 63.2 (s, $-O\underline{C}H_2\underline{C}H_2O-$), 125.0-133.0 (m, naphthyl group carbons), 133.2 (s, $\underline{C}H_2$=CH–), 134.9 (s, CH_2=$\underline{C}$H–), 166.4 (s, –O–$\underline{C}$O–CH_2– naphthyl), 171.9 ppm (s, CH_2=CH–$\underline{C}$O–O–).

Copolymer Synthesis

A series of copolymers of NAEA with AM and with VP was prepared to obtain reactivity ratios of the two copolymerizations and Q and e values of NAEA. The feed ratio of NAEA was varied from 10 to 80%. The copolymerizations of NAEA with AM were conducted at 65°C in DMF and at 40°C in DMSO. Tables

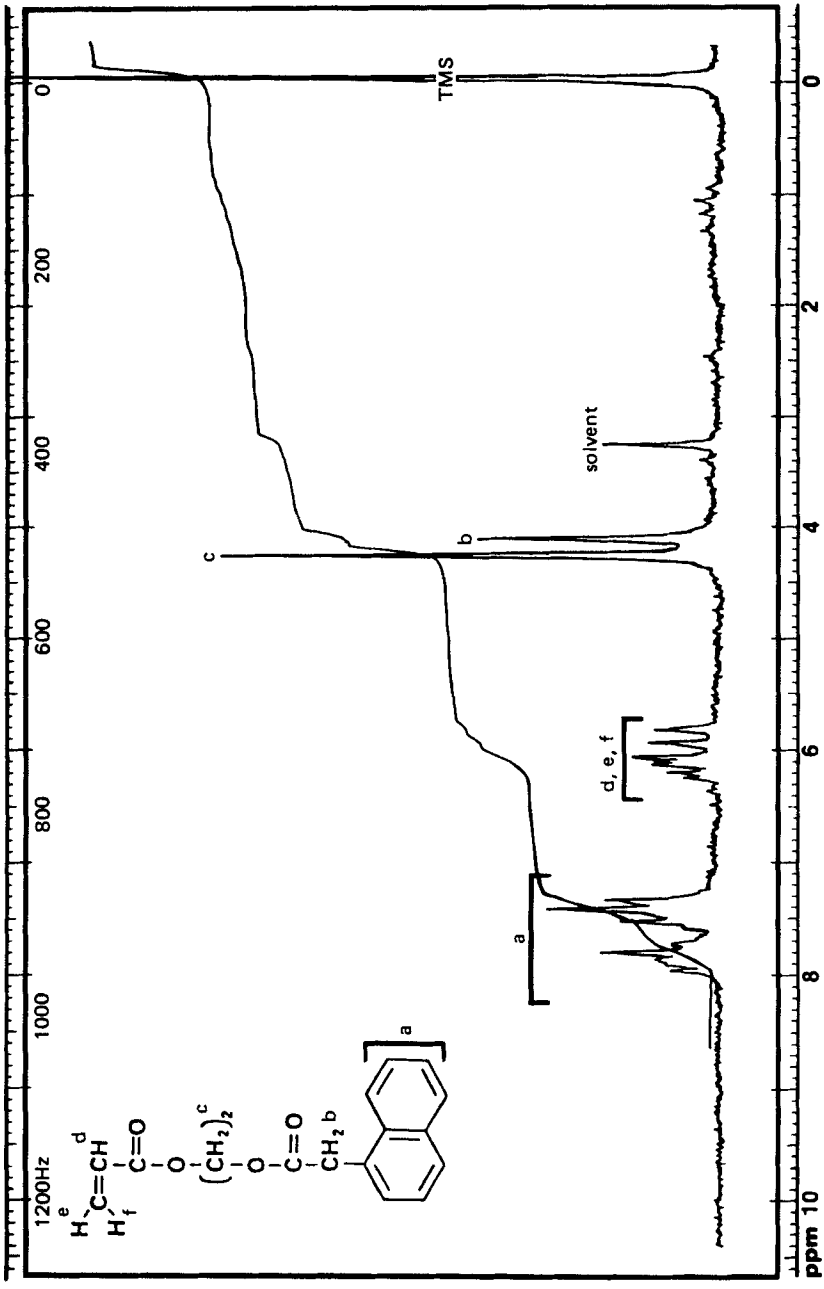

FIG. 1. ^{1}H-NMR spectrum of 2-(1-naphthylacetyl)ethyl acrylate.

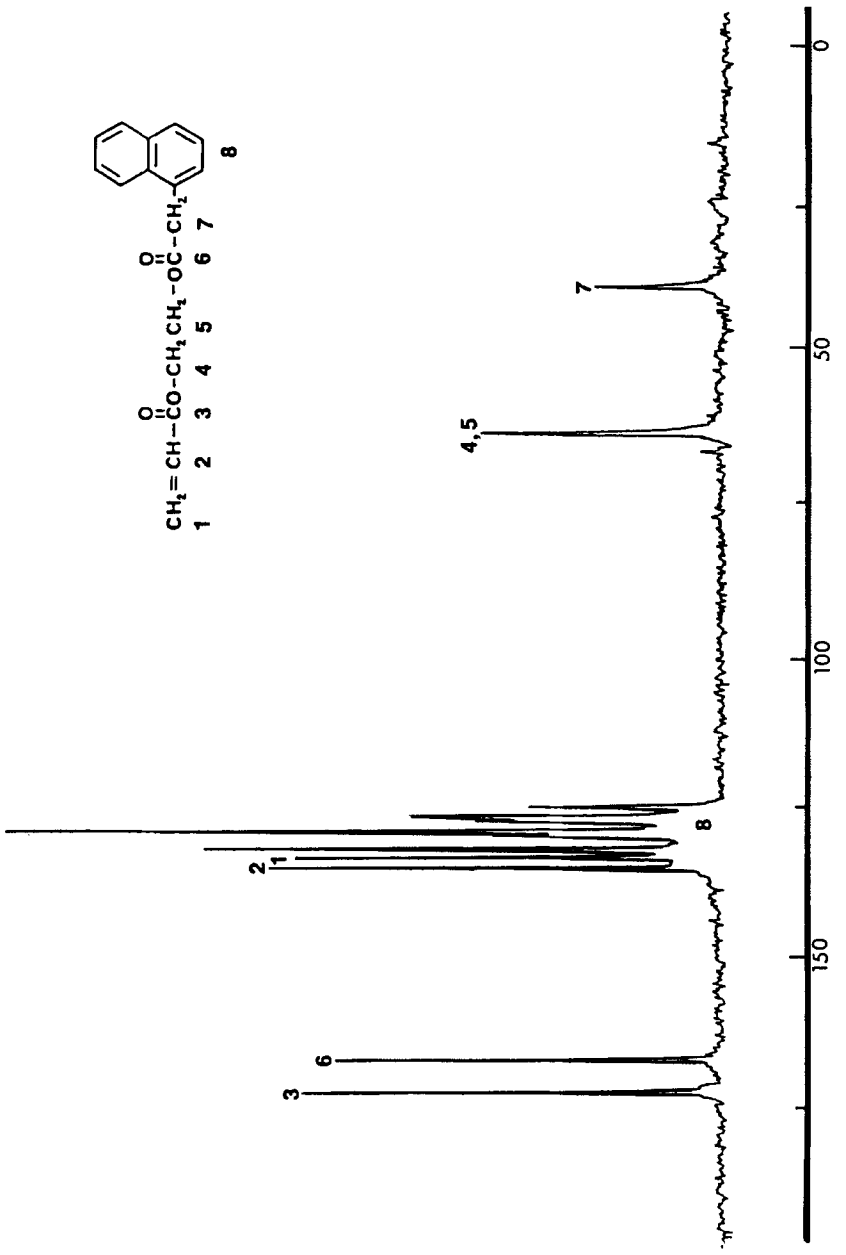

FIG. 2. ^{13}C-NMR spectrum of 2-(1-naphthylacetyl)ethyl acrylate.

TABLE 1. Reaction Parameters for the Copolymerization of NAEA (M_1) with AM (M_2) and Copolymer Composition[a]

Sample	Feed ratio, M_1:M_2	Reaction time, h	Conversion, %	Elemental analysis		M_1 in copolymer, mol%		
				C, %	N, %	EA	UV	NMR
NAEA-AM-1-1	1:9	0.5	12.9	51.85	12.46	9.8	12.3	9.3
NAEA-AM-2-1	2:8	0.3	8.2	–	–	–	21.7	24.2
NAEA-AM-3-1	3:7	0.3	7.8	54.21	5.41	33.9	29.9	–
NAEA-AM-4-1	4:6	0.3	5.8	–	–	–	44.6	–
NAEA-AM-5-1	5:5	0.3	5.2	66.64	3.49	53.1	54.1	49.5
NAEA-AM-6-1	6:4	0.3	7.0	–	–	–	59.2	–
NAEA-AM-7-1	7:3	1.0	13.6	70.20	1.80	71.4	71.8	–

[a]DMF, AIBN 0.25 mol%, 65°C.

TABLE 2. Reaction Parameters for the Copolymerization of NAEA (M_1) with AM (M_2) and Copolymer Composition[a]

Sample	Feed ratio, M_1:M_2	Reaction time, h	Conversion, %	M_1 in copolymer by UV, mol%
NAEA-AM-1-2	1:9	1.0	12.8	9.6
NAEA-AM-3-2	3:7	1.0	9.5	29.8
NAEA-AM-5-2	5:5	1.0	4.9	45.4
NAEA-AM-7-2	7:3	1.0	5.0	67.3

[a]DMSO, $K_2S_2O_8$ 0.10 mol%, 40°C.

1 and 2 list reaction parameters for the two copolymerization conditions, respectively. The copolymerizations of NAEA with VP were conducted at 60°C in DMF. Table 3 lists reaction parameters for the copolymerization of NAEA with VP.

Some copolymers of NAEA with hydrophilic comonomers were prepared for subsequent controlled-release work, and preparation conditions of these materials are shown in Table 4. AIBN and potassium persulfate were used as initiators, and the concentration of initiator was 0.1-1.0 mol% of the total monomer concentration in solution, 0.8 mol/L. Release performance of these polymers is described in an accompanying article [15].

As a typical example of the reaction procedure, the preparation of poly[2-(1-naphthylacetyl)ethyl acrylate-*co*-acrylamide], [NAEA(22.5)-AM], is described below. In 50 mL of freshly distilled DMF, 2.27 g (8 mmol) NAEA and 2.27 g (32 mmol) AM were dissolved and placed in a 100-mL, three-neck flask equipped with a nitrogen inlet tube, a rubber septum, and a condenser connected to a water trap. This mixture was purged with oxygen-free nitrogen for 15 min. Initiator dissolved in DMF was injected through the rubber septum. After a designated reaction time with continuous stirring, the resulting polymer was precipitated into 1000 mL anhydrous ethyl ether which contained a small amount of hydroquinone. The polymer was then dried under vacuum at room temperature. Conversion was determined gravimetrically. The polymer was further purified by precipitation from DMF solution with ethyl ether.

TABLE 3. Reaction Parameters for the Copolymerization of NAEA (M_1) with VP (M_2) and Copolymer Composition[a]

Sample	Feed ratio, M_1:M_2	Reaction time, h	Conversion, %	Elemental analysis		M_1 in copolymer, mol%	
				C, %	N, %	EA	UV
NAEA-VP-1-1	1:9	0.2	7.6	66.75	3.67	47.2	45.0
NAEA-VP-2-1	2:8	0.2	10.5	68.40	3.69	50.8	51.5
NAEA-VP-3-1	3:7	0.3	10.3	69.32	3.21	53.1	50.0
NAEA-VP-4-1	4:6	0.4	9.8	69.60	2.92	56.3	56.0
NAEA-VP-5-1	5:5	0.4	8.3	69.51	2.71	58.3	62.0

[a]DMF, AIBN 0.25 mol%, 60°C.

TABLE 4. Reaction Parameters for the Copolymerization of NAEA with Various Hydrophilic Comonomers

Copolymer	Feed ratio, NAEA:comonomer	NAEA in copolymer, mol%	Reaction solvent	Reaction temperature, °C	Initiator concentration, mol%	Reaction time, h	Conversion, %
NAEA-AM	2:8	22.5	DMF	65	AIBN (0.25)	4	63.0
NAEA-AM	3:7	30.9	DMSO	40	$K_2S_2O_8$ (0.1)	24	63.4
NAEA-MAA	2:8	20.5	DMSO	40	$K_2S_2O_8$ (0.1)	24	79.1
NAEA-HEMA	2:8	21.5	DMSO	40	$K_2S_2O_8$ (0.1)	24	84.4
NAEA-AA	2:8	23.7	DMSO	40	$K_2S_2O_8$ (0.1)	24	70.5
NAEA-VP	1:9	10.7	DOX[a]	65	AIBN (1.0)	5	85.3
NAEA-VP	2:8	25.0	DMF	60	AIBN (0.25)	5	73.2

[a]Dioxane.

Analytical Methods

Elemental analyses for carbon, nitrogen, and hydrogen of NAEA and the copolymers were conducted by M-H-W Laboratories of Phoenix, Arizona (Tables 1 and 3). The error in determination for each element was reported to be ±0.2%.

Viscosity measurements of the copolymers were performed in dimethylsulfoxide (DMSO) at 30°C with a Ubbelohde dilution capillary viscometer. The intrinsic viscosities were obtained by extrapolating the reduced viscosities and the inherent viscosities to zero concentration.

Membrane osmometry measurements were performed with a Knauer Osmometer in *N,N*-dimethylacetamide (DMAC) at 46.5°C, utilizing a 600W type membrane from Arro Laboratories.

The amount of residual monomer contained in the purified polymers was determined by a dialysis/LC method with DMSO.

IR spectra were recorded with a Perkin-Elmer 283B grating infrared spectrophotometer. UV spectra were obtained with a Perkin-Elmer 320 spectrophotometer. ^{1}H-NMR data were recorded with a Varian EM-360 NMR spectrometer, and ^{13}C-NMR spectra were obtained at 22.5 MHz on a JEOL FX-90Q spectrometer using 10-mm tubes.

RESULTS AND DISCUSSION

Reactivity Ratio Studies

Incorporation of hydrophilic comonomer units into polymer backbone significantly changes the polymer properties (especially hydrophilicity) and, accordingly, the release behavior. Hydrophilicity is known to be one of the major factors influencing release behavior of pendently attached polymeric controlled release systems. However, the incorporation of different comonomers also affects copolymer microstructure and neighboring group assistance. In this research we elucidate the effect of each parameter. Copolymerization studies were performed to get microstructural information through reactivity ratios of each comonomer.

In order to evaluate the effect of incorporation of comonomer units on the release (hydrolysis) properties, a series of copolymerizations was conducted with varying monomer feed ratios. The reaction parameters and the copolymerization results are listed in Tables 1, 2, and 3. The monomer feed ratios and the resultant copolymer compositions were used to calculate reactivity ratios for the NAEA-AM pair and the NAEA-VP pair.

TABLE 5. Reactivity Ratios for the Copolymerization of NAEA with AM and VP

Copolymerization conditions and r_1-r_2 calculation method	r_1	r_2	r_1r_2	Correlation coefficient
NAEA(M_1)-AM(M_2) (DMF, 65°C, AIBN);				
Fineman-Ross	1.00	0.86	0.86	0.983
Kelen-Tüdös	1.10	0.93	1.02	0.982
NAEA(M_1)-AM(M_2) (DMSO, 40°C, $K_2S_2O_8$):				
Fineman-Ross	0.84	1.03	0.86	0.993
Kelen-Tüdös	0.79	1.00	0.79	0.995
NAEA(M_1)-VP(M_2) (DMF, 65°C, AIBN):				
Fineman-Ross	0.43	0.02	0.01	0.997
Kelen-Tüdös	0.44	0.02	0.01	0.995

The Fineman-Ross method [16] and the Kelen-Tüdös method [17] were employed to determine the monomer reactivity ratios at low conversion. The Fineman-Ross plot for NAEA (M_1) and AM (M_2) yields reactivity ratios of $r_1 = 1.00$ and $r_2 = 0.86$ (at the polymerization conditions of DMF, 65°C, and AIBN). A plot of the data according to the Kelen-Tüdös method gives values of 1.10 and 0.93 (DMF, 65°C, and AIBN) for r_1 and r_2, respectively. On the other hand, both of the methods yield reactivity ratios of $r_1 = 0.44$ and $r_2 = 0.02$ for NAEA (M_1) and VP (M_2).

A comparison of the reactivity ratios obtained by the two low-conversion methods for NAEA(M_1)-*co*-AM(M_2) and NAEA(M_1)-*co*-VP(M_2) is given in Table 5, which shows that monomer reactivity ratios are not independent of the reaction conditions in radical copolymerization [18]. Different r_1 and r_2 values were obtained for NAEA(M_1)-*co*-AM(M_2) for two sets of polymerization conditions.

Figure 3 shows the copolymer composition as a function of feed composition for the copolymerization of NAEA with AM and that of NAEA and VP. The NAEA(M_1)-AM(M_2) pair exhibits a random tendency in copolymerization since the reactivity ratios are both near unity and $r_1r_2 = 0.94$. On the other hand, the NAEA(M_1)-VP(M_2) pair (r_1 and r_2 both less than unity and

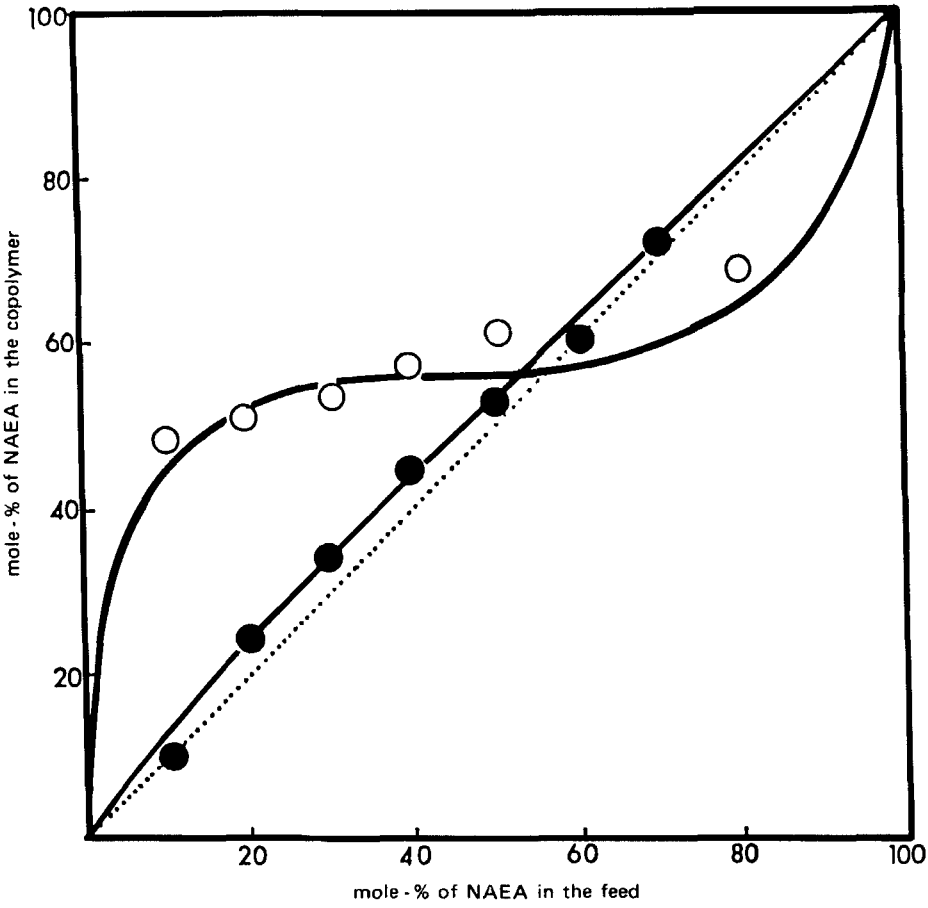

FIG. 3. Copolymer composition as a function of feed composition for the copolymerization of NAEA with AM (DMF, AIBN, 65°C) (●) and for the copolymerization of NAEA with VP (○). The dotted line represents ideal random copolymerization.

$r_1 r_2 = 0.01$) possesses almost perfectly alternating tendency in copolymerization. In the NAEA-VP copolymerization the azeotropic copolymerization point occurs at approximately 50 mol% of each monomer in the feed.

TABLE 6. Q and e Values of NAEA[a]

Comonomer pair	Polymerization conditions	Q	e
NAEA(M_1)-AM(M_2)	DMF, 65°C, AIBN	0.94	0.99
	DMSO, 40°C, $K_2S_2O_8$	0.74	0.80
NAEA(M_1)-VP(M_2)	DMF, 60°C, AIBN	0.66	1.07
Average		0.78 ± 0.14	0.95 ± 0.14

[a]Where $r_1 = (Q_1/Q_2) \exp [-e_1(e_1 - e_2)]$.
$r_2 = (Q_2/Q_1) \exp [-e_2(e_2 - e_1)]$.

Q and e Values of NAEA Monomer

The Q and e values of NAEA were calculated from the reactivity ratios obtained by the two low-conversion methods and the known Q and e values of AM and VP [19], giving $Q = 0.78 \pm 0.14$ and $e = 0.95 \pm 0.14$ by using the Q-e scheme [20, 21]. A comparison of Q and e values for NAEA obtained under different copolymerization conditions is given in Table 6. These Q and e values of NAEA can be used to predict reactivity ratios for other comonomer pairs without the necessity of experimental measurement.

Copolymer Macrostructure and Properties

The homopolymer of NAEA is expected to be difficult to hydrolyze due to its hydrophobic nature. Therefore NAEA was copolymerized with hydrophilic comonomers to enhance the hydrolysis of the auxin-polymer linkage. It is anticipated that the copolymers containing moderately high portions of hydrophilic comonomer would be promising candidates for controlled release. The copolymers used for release studies were prepared with 10 to 30 mol% of auxin monomer (NAEA).

The structures of the copolymers were verified by IR, UV, ^{13}C NMR, and elemental analysis. The procedure for determining copolymer compositions by ^{13}C NMR is discussed in detail elsewhere [22, 23]. Briefly, the carbonyl peaks were used as a standard, and naphthyl peaks (120-130 ppm in Fig. 4) were integrated to give the mole percent of NAEA in the copolymer. The copolymer compositions, as determined by ^{13}C NMR, are shown in Table 1 and

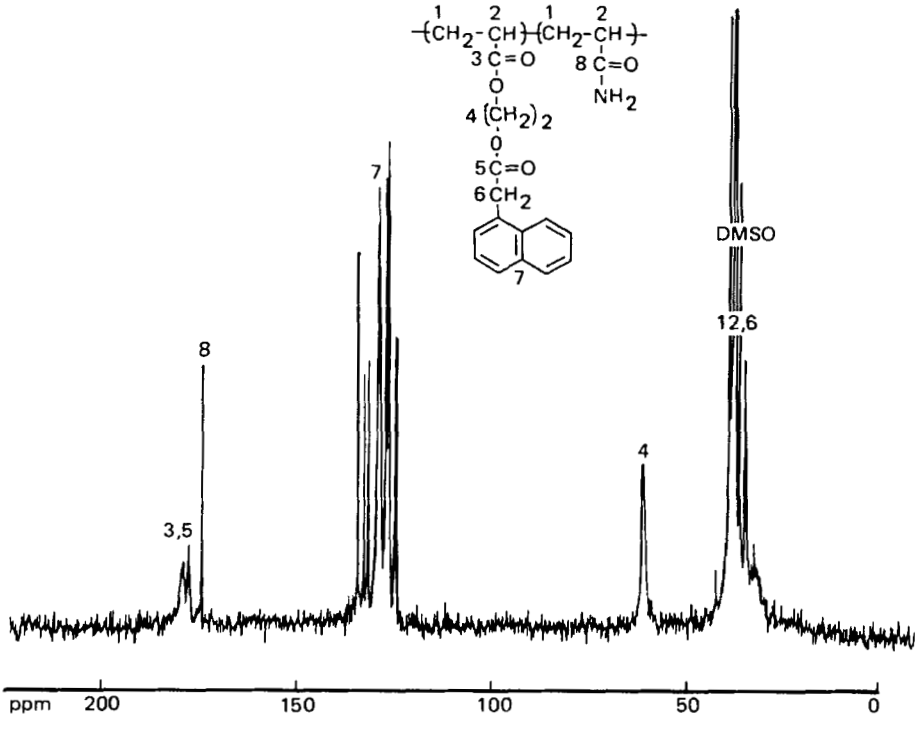

FIG. 4. A typical ^{13}C-NMR spectrum of a copolymer of 2-(1-naphthylacetyl)-ethyl acrylate with acrylamide.

agree favorably with the compositions determined from elemental analysis and UV spectroscopy. Typical ^{13}C-NMR spectra of a copolymer of NAEA with AM and that of NAEA with VP are shown in Figs. 4 and 5, respectively.

Residual monomer contents of all polymers are below 0.1 mol% of available NAA, except for the NAEA (21.5)-HEMA sample (0.3 mol%). Molecular weights are between 50 000 and 140 000, corresponding to degrees of polymerization of 250-700 (Table 7).

Copolymer Microstructure

The influence of copolymer microstructure on the release properties is very important in the design of controlled-release polymeric systems, particularly when catalytic effects of the neighboring group are utilized to facilitate

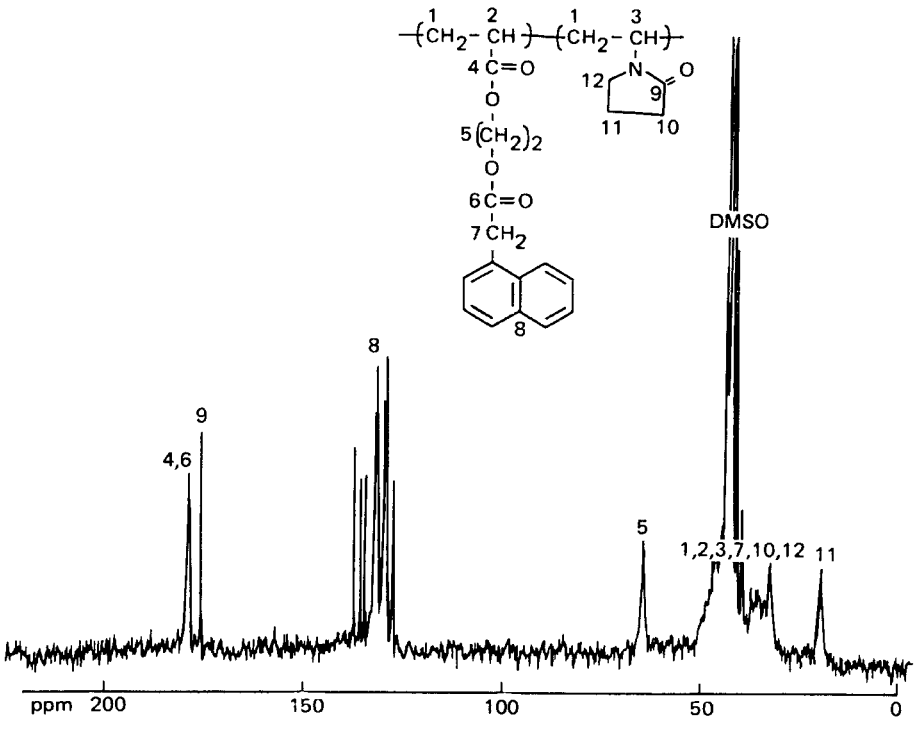

FIG. 5. A typical ^{13}C-NMR spectrum of a copolymer of 2-(1-naphthylacetyl)ethyl acrylate with *N*-vinyl-2-pyrrolidone.

hydrolysis. The statistical copolymer microstructure was obtained from the reactivity ratios r_1 and r_2 calculated from the *Q-e* values in Table 8.

Microstructural calculations were carried out to estimate the degree of blockiness and alternation in the copolymers. The statistical distribution of monomer sequences M_1-M_1, M_2-M_2, and M_1-M_2 was calculated by the method of Igarashi [24]. Monomer sequence lengths, μ_1 and μ_2, were also calculated from the reactivity ratios for the comonomer pairs [25]. Tables 9 and 10 list the results.

The mean sequence lengths for the NAEA-AM system vary considerably with the composition (Table 9); those for the NAEA-VP system remain almost unchanged (Table 10). Nearly identical mean sequence length values are a further indication of the alternating tendency in the NAEA-VP copolymers.

TABLE 7. Properties of Auxin-Containing Copolymers

Copolymer	$[\eta]$, dL/g	$\bar{M}_n \times 10^{-4}$	Residual NAEA content, mol%[a]
NAEA(22.5)-AM	0.29	5.1	<0.1
NAEA(30.9)-AM	0.44	9.0	<0.1
NAEA(20.5)-MAA	0.53	14.0	<0.1
NAEA(21.5)-HEMA	1.02	–	0.3
NAEA(23.7)-AA	0.35	–	<0.1
NAEA(10.7)-VP	0.20	–	<0.1
NAEA(25.0)-VP	0.28	6.2	<0.1

[a]Mol% of totally incorporated NAEA.

TABLE 8. Q and e Values of the Related Monomers

Monomer	Q	e
Acrylamide (AM)[a]	1.12	1.19
N-Vinyl-2-pyrrolidone (VP)[a]	0.14	-1.14
Methacrylic acid (MAA)[a]	2.34	0.65
Acrylic acid (AA)[a]	1.15	0.77
2-Hydroxyethyl methacrylate (HEMA)[b]	0.93	0.40
2-(1-Naphthylacetyl)ethyl acrylate (NAEA)[c]	0.78	0.95

[a]From Ref. 19.

[b]From R. H. Yocum and E. B. Nyquist, *Functional Monomers*, Vol. 1, Dekker, New York, 1973, p. 308.

[c]Calculated from experimentally obtained r_1 and r_2 values in this work.

TABLE 9. Structural Data for the Copolymers of NAEA-AM[a]

Sample	Composition		Blockiness		Alternation, NAEA-AM	Mean sequence length	
	NAEA	AM	NAEA-NAEA	AM-AM		μ_{NAEA}	μ_{AM}
NAEA-AM-1-1	9.80	90.20	0.98	81.38	17.65	1.12	9.33
NAEA-AM-3-1	33.90	66.10	11.60	43.80	44.30	1.47	3.16
NAEA-AM-5-1	53.10	46.90	28.33	22.13	49.55	2.10	1.93
NAEA-AM-7-1	71.40	28.60	51.07	8.27	40.66	3.58	1.40

[a]Composition, blockiness, and alternation in mol%.

TABLE 10. Structural Data for the Copolymers of NAEA-VP[a]

Sample	Composition		Blockiness		Alternation, NAEA-VP	Mean sequence length	
	NAEA	VP	NAEA-NAEA	VP-VP		μ_{NAEA}	μ_{VP}
NEAE-AP-1-1	47.2	52.8	1.84	7.36	90.80	1.05	1.14
NAEA-VP-3-1	53.1	46.9	7.87	1.71	90.42	1.18	1.04
NAEA-VP-5-1	58.2	41.8	17.15	0.65	82.20	1.43	1.02

[a]Composition, blockiness, and alternation in mol%.

TABLE 11. Structural Data for the Auxin Copolymers of Different Comonomer Combinations[a]

Copolymer	Blockiness		Alternation,	Mean sequence length	
	M_1-M_1	M_2-M_2	M_1-M_2	μ_{M_1}	μ_{M_2}
NAEA(22.5)-AM	4.20	64.08	31.72	1.27	5.04
NAEA(30.9)-AM	8.59	48.29	43.12	1.40	3.24
NAEA(20.5)-MAA	1.01	80.17	18.83	1.11	9.52
NAEA(21.5)-HEMA	3.82	58.99	37.18	1.21	4.17
NAEA(23.7)-AA	3.97	63.51	32.32	1.24	4.94
NAEA(10.7)-VP	2.19	8.08	89.73	1.05	1.18
NAEA(25.0)-VP	5.02	3.65	91.32	1.11	1.08

[a]NAEA content, blockiness, and alternation in mol%.

Table 11 lists the calculated statistical data for copolymers with different comonomer combinations used for subsequent release studies. These are expected to be quite accurate for the polymers of low conversion. The effects of compositional drift at high polymer conversions cannot be ignored, but the general trend among copolymer systems should be maintained. The mean sequence lengths for poly(NAEA-*co*-VP) are 1.0-1.1 for both comonomer units regardless of feed composition. Alternation percentage of 90 ± 1 for both feed ratios demonstrates an almost perfectly alternating tendency of poly(NAEA-*co*-VP). Poly(NAEA-*co*-MAA) shows less blockiness of NAEA units. The other copolymer systems, poly(NAEA-*co*-HEMA) and poly(NAEA-*co*-AA), show similar trends of relatively random nature in copolymerization and polymer microstructure.

CONCLUSIONS

The auxin-containing monomer NAEA was synthesized via a PPY-catalyzed DCC method. Copolymers of NAEA with hydrophilic comonomers (AM, VP, MAA, HEAM, and AA) were prepared. Elemental analysis, IR, UV, and NMR were used to determine copolymer macrostructure. Molecular weights were

estimated by intrinsic viscosity and membrane osmometry measurements. The reactivity ratios, $r_1 r_2$ = 0.94 for NAEA-AM copolymers and $r_1 r_2$ = 0.01 for NAEA-VP copolymers, were determined from the two low-conversion methods and indicate the tendency of the NAEA-AM pair toward random and the NAEA-VP pair toward alternating copolymerization behavior. Q and e values of NAEA monomer were determined to be 0.78 and 0.95, respectively. Statistical microstructure was obtained from the reactivity ratios calculated theoretically from the Q-e scheme. This information is utilized to investigate the influence of copolymer microstructure on the release properties in a subsequent paper [15].

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