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COPOLYMERIZATION STUDY OF 4-VINYLPYRIDINE WITH *N*-DODECYLACRYLAMIDE

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Abstract—Random copolymers of 4-vinylpyridine and *N*-dodecylacrylamide were synthesized by low conversion bulk free radical copolymerization using 2,2′-azobisisobutyronitrile as initiator. Copolymer compositions were obtained from NMR spectrometry and elemental analysis. The reactivity ratios r_{VP} and $r_{C_{12}AM}$ as determined from the Fineman–Ross, Kelen–Tüdos and Mayo–Lewis methods were found to be 4.13 and 0.27, respectively. The examination of the C-4 resonance peak in ^{13}C NMR data reveals a triad effect. A good agreement was observed for the experimental triads fractions determination and their calculation from r_{VP} and r_{C12}. © 1997 Elsevier Science Ltd

INTRODUCTION

Acrylamide based water-soluble copolymers have been the subject of numerous investigations opening wide possibilities of applications in many fields. When the comonomer is 4-vinylpyridine, the corresponding copolymers, the poly(acrylamide-*co*-4-vinylpyridine)s are described as new chemical materials in the field of metallopolymers [1]. Indeed, treatment of the copolymers with Ru(II), gives rise to ruthenium bipyridyl complexes which form interesting redox catalysts for solar energy conversion [2]. In the case of the copolymerization of a hydrophobic acrylamide (e.g. *N*-dodecylacrylamide) with 4-vinylpyridine, the poly(*N*-dodecylacrylamide-*co*-4-vinylpyridine)s with a variable hydrophilic/hydrophobic balance are interesting precursor polymers for the preparation of new amphiphilic cationic polymers after quaternization of the pyridine rings. The physicochemical properties (e.g. the viscosity, the ability to solubilize hydrocarbons, the micelle-like microphase formation and the interfacial tension properties) are strongly dependent on their microstructure. In order to establish a relationship between the molecular structure and the aqueous solution behaviour of these amphiphilic polymers, we have synthesized a series of precursors with variable compositions allowing the determination of the reactivity ratios of the two comonomers (*N*-dodecylacrylamide and 4-vinylpyridine).

This paper reports the results concerning the calculation of the monomers reactivity ratios using Fineman–Ross, Kelen–Tüdos and Mayo–Lewis methods. On the basis of a statistics–kinetics model, these ratios allow the determination of the different sequences distributions (triads) and microstructural information.

EXPERIMENTAL

4-Vinylpyridine (4-VP) is a commercial product from Aldrich containing 100 ppm of hydroquinone as polymerization inhibitor. This monomer was distilled under reduced pressure in the presence of calcium hydride by transfer on a cold condensing surface ($T = 30°C$, 2 mm Hg).

N-Dodecylacrylamide ($C_{12}AM$) was prepared by reaction of the acryloyl chloride with *n*-dodecylamine [3]. *N*-Dodecylacrylamide was purified twice by recrystallization from heptane (heating remaining below 50°C for dissolution), then the solution was slowly cooled down to 0°C. As an ultimate purification the monomer was purified by chromatography on silica gel or alumina column with ethyl acetate as the eluent ($R_f = 0.85$ or 0.8, respectively). Mp = 58°C, Ref. [3] = 55.5–56.5°C.

The copolymerizations of $C_{12}AM$ with 4-VP were carried out in bulk at 70°C with AIBN as a free radical initiator and by varying the feed ratios in monomers (Table 1). The iniator content was fixed at 0.53% (molar per cent/monomers) and the total amount of monomers was equal to 3×10^{-2} mol. The reactor was deoxygenated under vacuum by repeating the freeze–thaw cycles several times. After degassing the reactor was purged with argon.

The copolymer was recovered by dissolution in a minimum of chloroform (0.2–0.4 ml/g) and the solution was then loaded on a silica gel column using ethyl acetate as an eluent in order to eliminate the monomers. The adsorbed polymer was then recovered by washing the column with chloroform. The copolymer was dried *in vacuo* for 48 hr at room temperature. Copolymer compositions were determined either from elemental analysis or ^1H NMR by integration of methylene and methyl peaks. ^1H NMR spectra were obtained using deuterochloroform copolymer solutions, with a AC-200P Bruker spectrometer. The ^{13}C NMR spectra were recorded on the same spectrometer operating at 50.327 MHz using the standard inverse gated microprogramme. The proton broad band irradiation was performed by using the composite pulses CPD:spectra width 12,500 Hz, acquisition time 0.655 sec, pulse delay 12 sec and number of scans 3607.

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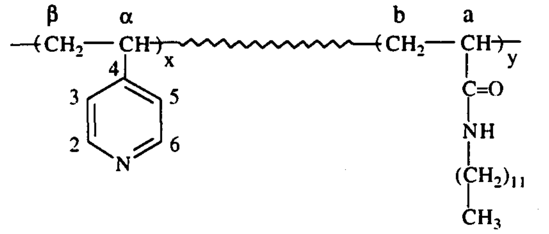

Scheme. 1. Poly(*N*-dodecylacrylamide-*co*-4-vinylpyridine)s.

RESULTS AND DISCUSSION

As the properties of the copolymers in aqueous solution are dependent on the distribution of the hydrophilic units and of the hydrophobic ones in the macromolecules, it is of interest to examine the microstructure of the copolymers. Accordingly, we have determined the parameters r_{VP} and r_{AM} representing the monomer reactivity ratios for 4-VP and *N*-dodecylacrylamide, respectively. The calculation of these ratios based on the comparison between monomer conversion and copolymer composition was carried out using the methods developed by Kelen–Tüdos [4], Fineman–Ross [5], and the non-linear least squares one [6] by hypothesizing that, in most cases, a polymer chain growing depends only on the nature of the active extremity (terminal model).

By denoting f_{VP}, f_{AM}, F_{VP} and F_{AM} the instantaneous molar fractions of the units 4-VP and C_{12} in the feed and incorporated in the polymer, respectively, the polymer chemical forming composition is given by the differential form of the copolymerization equation:

$$\frac{d[VP]}{d[C_{12}AM]} = \frac{F_{VP}}{F_{C_{12}AM}} = \frac{f_{VP}}{f_{C_{12}AM}} = \frac{r_{VP}f_{VP} + f_{C_{12}AM}}{r_{C_{12}AM}f_{C_{12}AM} + f_{VP}}$$

From a refined linearization method (KT), this equation can be expressed by:

$$\eta = \left(r_{VP} + \frac{r_{C_{12}AM}}{\alpha} \right)\xi - \frac{r_{C_{12}AM}}{\alpha} \qquad (1)$$

with

$$x = \frac{F}{\alpha + F} h = \frac{G}{\alpha + F}$$

The parameter α is calculated by taking the square root of the product $F_{min}F_{max}$, where F_{min} and F_{max} are the lowest and highest values of F for the copolymerization. The reactivity ratios r_{VP} and $r_{C_{12}AM}$ were calculated from the slope and the intercept of the line representing relation (1).

The data are gathered in Table 1 and the corresponding plot is shown in Fig. 1.

Moreover, from the solutions of the equation expressing the instantaneous copolymer compositions, F_{VP} as a function of the initial comonomer feed composition f_{VP}, it is clear that the calculated curve is in good agreement with the experimental results (Fig. 3).

The monomers reactivity ratios were also estimated by the Fineman–Ross method by using a least-squares fit to give $r_{VP} = 3.96$ and $r_{C_{12}AM} = 0.23$ with a correlation coefficient equal to 0.999 (Fig. 2). These values were found to be slightly lower than those from other treatments (Table 2).

Looking at these results, we observe an enrichment in 4-VP starting from initial feeds superior to 49%. Indeed, the high value for the 4-VP reactivity ratio indicates a tendency for this monomer to homopolymerize, while in contrast the low value for $C_{12}AM$ shows a tendency of the second monomer to copolymerization. These results also suggest that the distribution of the two monomers in the copolymers is of a block character with high content of the 4-VP monomer.

The final copolymer composition was determined by integration of the peaks corresponding to the

Table 1. Monomer reactivity ratios of 4-vinylpyridine (VP) with *N*-dodecylacrylamide ($C_{12}AM$)

Method	r_{VP}	$r_{C_{12}AM}$
Kelen–Tüdos	4.13 ± 0.1	0.27 ± 0.01
Mayo–Lewis	4.66 ± 0.1	0.32 ± 0.02
Fineman–Ross	3.96 ± 0.15	0.23 ± 0.02

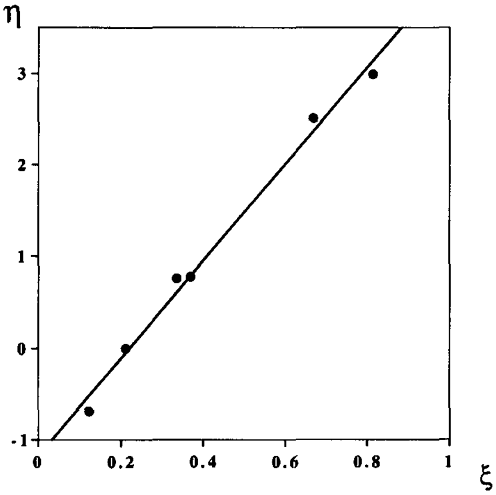

Fig. 1. Kelen–Tüdos plot for the 4-VP/C_{12}AM system ratios for the copolymerization.

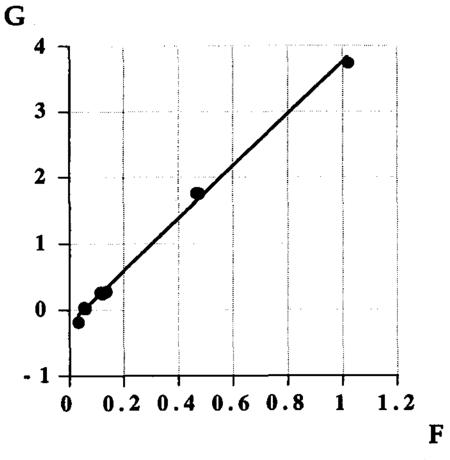

Fig. 2. Determination of reactivity ratios for the copolymerization of 4-VP with C_{12}AM by the Fineman–Ross method.

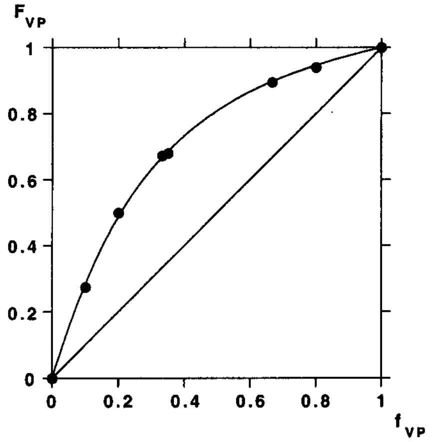

Fig. 3. Instantaneous copolymer composition F_{VP} as a function of the initial comonomer feed composition f_{VP} for the copolymerization of 4-VP with $C_{12}AM$.

protons of the pyridine rings and the characteristic ones of the acrylamide chains (Fig. 4):

pyridine ring $H_2 + H_6$ $\delta_1 = 8.35$ ppm
$H_3 + H_5$ $\delta_2 = 6.43$ ppm
methyl group of the C_{12} chain $\delta_{CH_3} = 0.9$ ppm
methylene group in a of NH $\delta_{CH_2} = 3$ ppm

The resonance peak of the secondary amide side chain proton is overlapped by H-3 and H-5, consequently, only H-2 and H-6 will be taken into account.

It should be possible to determine the polymer composition from ^{13}C NMR ($CHCl_3$ solutions). Indeed, distinctive chemical shifts for each block can be derived from the ^{13}C NMR spectra of the two constitutive homopolymers (poly 4-VP and poly $C_{12}AM$):

$C_{12}AM$ unit
$\delta_{C=0} = 175$ ppm $\delta_{CH_2(b) = 23\ ppm}$
$\delta_{CH_3} = 14$ ppm $\delta_{CH}(a) = 43$ ppm

4-VP unit
$\delta_{C_2+C_6} = 150\text{–}152$ ppm $\delta_{CH_2}(b) = 44$ ppm
$\delta_{C_3+C_5} = 120\text{–}126$ ppm $\delta_{CH}(a) = 40$ ppm
$\delta_{C_4} = 153$ ppm

However, for copolymers with a low $C_{12}AM$ content, the peak area related to the carbonyl group appears too weak to be integrated with an acceptable precision. Therefore, the most reliable results for the copolymer composition were obtained from the

Table 2. Copolymerization of 4-vinylpyridine with *N*-dodecylacrylamide

Initial concentration VP (10^{-3} mol)	Initial concentration $C_{12}AM$ (10^{-3} mol)	f_{VP}	Reaction time (min)	Conversion (%)	F_{VP}
24	6	0.8	10	4	0.94
20	10	0.667	10	7	0.895
10.8	20	0.35	22	7	0.68
10	20	0.333	30	10	0.68
6	24	0.2	20	3.1	0.499
3	27	0.1	25	2	0.274

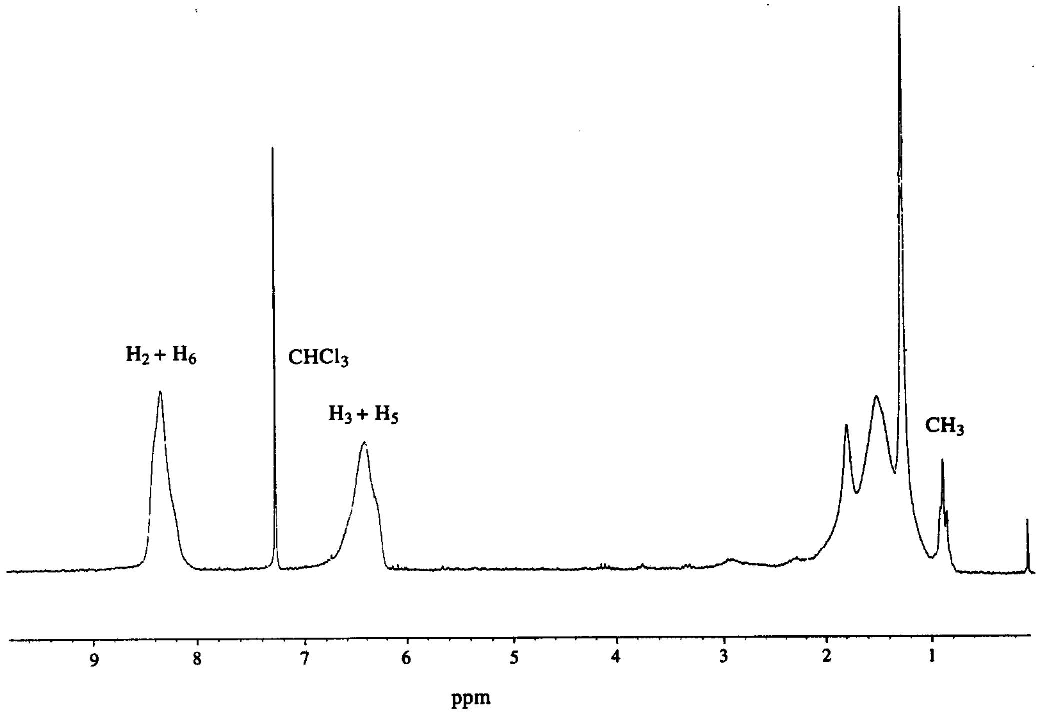

Fig. 4. ^1H NMR spectra of 4-VP and dodecylacrylamide copolymer (88% 4-VP, 12% $C_{12}AM$) (solvent: $CDCL_3$).

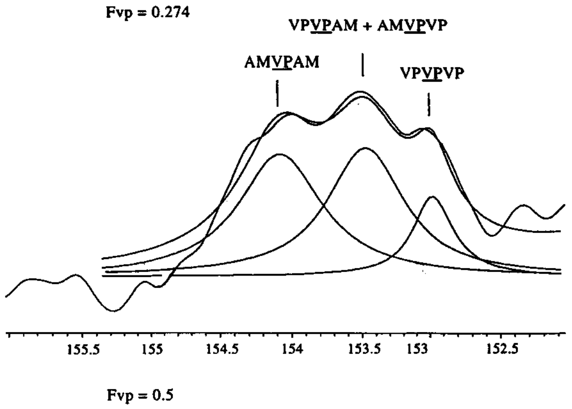

Fig. 5. C-4 resonance peaks of 4-vinylpyridine units incorporated in 4-vinyl/*N*-dodecylacrylamide copolymers: decomposition into lorentzian singlets.

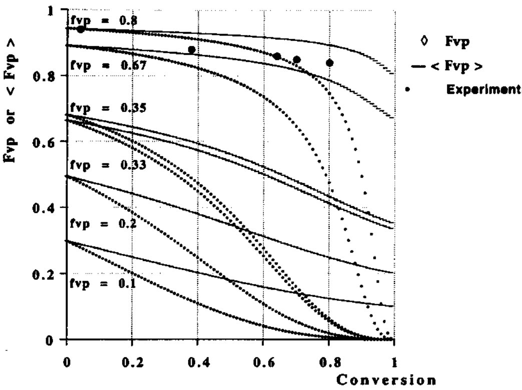

Fig. 6. Dependence of the overall average $\langle F_{VP} \rangle$ and the instantaneous copolymer composition F_{VP} on the conversion of 4-VP.

resonance peak areas of the methyl groups (acrylamide chain) and of the pyridine ring protons. Our copolymers ^{13}C NMR spectra show a variation of the $C_2 + C_6 + C_4$ and $C_3 + C_5$ peaks profiles at 150–156 ppm and 120–126 ppm, respectively, as a function of the comonomers composition. This phenomenon is due to the sensitivity of these carbons to the local chemical environment. Despite a low resolution, we can observe for C-4 of the pyridine ring, two or three peaks, as shown in Fig. 5, which are assigned by comparison with the ^{13}C NMR of 4-VP/styrene copolymers [7], to the VP-centered triads VP$\underline{\text{VP}}$VP, VP$\underline{\text{VP}}$AM + AM$\underline{\text{VP}}$VP and the triad AM$\underline{\text{VP}}$AM. From the expanded ^{13}C NMR spectra of C-4, we have determined the fractions of the VP-centered triads. The measurements were carried out on three samples, with F_{VP} values equal to 0.274, 0.5, and 0.94, respectively, by decomposition of the C-4 resonance experimental peak in three lorentzian singlets (Fig. 5). The results collected in Table 3 are in good agreement with those obtained from the statistical stationary process given by Coleman [8] and developed by Ito [9].

From the terminal model, the mean length of the monomers sequences were calculated from the reactivity ratios at low conversion, $F_{VP} = 0.274$, $\mu_{VP} = 16.9$, $\mu_{AM} = 1.1$; $F_{VP} = 0.5$, $\mu_{VP} = 1.98$, $\mu_{AM} = 2.1$; $F_{VP} = 0.94$, $\mu_{VP} = 1.44$, $\mu_{AM} = 3.54$.

Another point of this study is the analysis of the copolymer composition as a function of the conversion yield. The composition was determined from the reactivity ratios r_{VP} and $r_{C_{12}AM}$ and by taking the experimental values f_{VP}. The instantaneous copolymer composition F_{VP} and the average copolymer composition $\langle F_{VP} \rangle$ were calculated for $F_{VP} = 0.1$, 0.2, 0.33, 0.35, 0.67 and 0.8, and the variation of the compositions was plotted as a function of the conversion ratios (Fig. 6). From these curves, we observe that for high initial 4-VP compositions in the feed ($F_{VP} = 0.67$, 0.8), the average copolymer composition is close to the instantaneous one. For the highest F_{VP} value (0.8), no large drift was observed up to a 60% conversion ratio. For $F_{VP} = 0.8$, the experimental values $\langle F_{VP} \rangle$ were calculated from elemental analysis.

Table 3. 4-Vinylpyridine centred triads distribution

	$F_{VP} = 0.274$			$F_{VP} = 0.5$			$F_{VP} = 0.94$		
Triads	δ (ppm)	Calcd	Exp.	δ (ppm)	Calcd	Exp.	δ (ppm)	Calcd	Exp.
VPVPVP	153	0.09	0.14	152.9	0.244	0.233	152.6	0.885	0.878
VPVPAM + AMVPVP	153.5	0.42	0.427	153.4	0.5	0.574	153.2	0.111	0.122
AMVPAM	154.1	0.48	0.43	154.8	0.256	0.193	—	0.003	—

Calcd: Calculated with $r_{AM} = 4.13$ and $r_{VP} = 0.27$. Exp.: Determined from ^{13}C NMR.

CONCLUSION

Studies were made on the free radical copolymerization of 4-vinylpyridine with *N*-dodecylacrylamide. ^{1}H NMR was used to determine the copolymers compositions. Reactivity ratios found to have $r_{VP}r_{AM} = 1.1$ indicate that the growing polymer chains incorporate 4-VP more easily. The statistically predicted copolymers sequence distributions (4-VP centred triads) were confirmed by ^{13}C NMR.

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