Copolymers of Vinylamine and Vinylalcohol by Acid Hydrolysis of Poly(N-Vinyl-tert-Butylcarbamate-co-Vinylacetate): Evaluation of Reactivity Ratios

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Synopsis

Copolymers of vinylamine and vinylalcohol were prepared by hydrolysis of poly(N-vinyl-tert-butylcarbamate-co-vinylacetate) in 1:1 v/v % ethanol/HCl mixtures at room temperature. Reactivity ratios of the monomers N-vinyl-tert-butylcarbamate (1) and vinylacetate (2) were calculated from monomer feed and copolymer composition data, according to the methods of Fineman–Ross and Kelen–Tüdös, yielding $r_1 = 1.14 \pm 0.05$, $r_2 = 0.47 \pm 0.07$, and $r_1 = 1.12 \pm 0.07$, $r_2 = 0.46 \pm 0.03$, respectively. From these values the average sequence length distribution of monomer units was derived showing that in the reaction of N-vinyl-tert-butylcarbamate and vinylacetate nearly Bernouillian (i.e., purely random) copolymers are formed, with a slight tendency toward alternation.

INTRODUCTION

The polymeric amine with the simplest chemical structure is undoubtedly poly(vinylamine) and although its synthesis is rather laborious, it can be prepared according to one of the synthetic routes already known.[1–5]

Some important features of these polymers are their water solubility, complexation properties toward transition metal ions,[6] rather high basicity of the amine groups (pK_a $(-\mathrm{NH_3^+}) \approx 9$),[7] and the capability of easy reaction with all kinds of electrophilic compounds, such as dyes.[4] The pH-dependent basicity of amine groups is of fundamental scientific interest.[8]

In our laboratory poly(vinylamine) is being used as a functional polymeric ligand of a thiol oxidation catalyst. Application of this polymeric base instead of NaOH was found to increase catalytic activity 50-fold.[9] It appeared from viscosity,[10] pH,[11] and kinetic[12] measurements that the amine group basicity, polymer charge, and conformation largely affected catalytic acitivity. Combination of these properties with other desirable functionalities can be achieved by appropriate copolymerization. Selection of the synthetic route will depend on the nature of the comonomer.

Copolymers of vinylamine and a suitable uncharged comonomer seem to offer the opportunity to investigate the effect of base group density within the polymer chain on catalytic activity.

For this purpose copolymers with either randomly distributed vinylamine units or alternating monomer units are preferred to block copolymers.

Until now, to our knowledge, the synthesis of only two water-soluble vinyl

copolymers containing vinylamine has been reported: copolymers of vinyl-amine with sodium vinylsulfonate, containing cationic and anionic func-tionalities in water,[13] and copolymers of vinylamine with vinylalcohol, con-taining only cationic functionalities. The latter copolymers were prepared first by Nikolayev[14] starting from copolymers of vinylphthalimide and vi-nylacetate, which could be aminolyzed and hydrolyzed, respectively, with hydrazine hydrate. Decomposition of the formed phthalylhydrazide salt of vinylamine was achieved in hydrochloric acid according to the method of Reynolds and Kenyon.[1] Very recently, a new way of preparing copolymers of vinylamine and vinylalcohol, by acid hydrolysis of copolymers of N-vinyl-tert-butylcarbamate (NVTBC) and vinylacetate (VAc), based on the Hart synthesis of polyvinylamine[15] was outlined briefly by Bloys van Treslong and Jansen.[16] The synthetic route they described is an important contri-bution to making these copolymers more accessible to further investigations. Unfortunately, little copolymerization data were presented, thus prohib-iting accurate calculation of the reactivity ratios of the pre-monomers. Therefore, we followed their preparation method successfully (with minor modifications) and determined the copolymer reactivity ratios of the mon-omers from completive data to get insight into the randomness of these very hygroscopic copolymers.

EXPERIMENTAL

Synthesis of the Pre-Copolymers

NVTBC was synthesized according to the Hart method,[15] with some minor modifications.[17] After drying thoroughly, the white, powdery NVTBC was purified by sublimation at 54°C at 1 kPa pressure. Because of the highly poisonous character of NVTBC—in aquo the toxic hydrolysis product ethy-lenimine is formed—all manipulations with this reagent were carried out under an efficient fume hood. VAc (kindly provided by DSM) was vacuum distilled before use.

Copolymerization of NVTBC and VAc was carried out in benzene (Merck pro analysi, dried on CaH_2) at 60°C for 6 h with α, α'-azoisobutyronitrile as initiator under nitrogen. The pre-copolymers were isolated by precipitating the reaction product in a 20-fold excess of ice-cold n-hexane. After drying, the copolymers were purified by redissolution in toluene and precipitation in n-hexane, followed by washing with n-heptane (pro analysi) to remove residual initiator. The purified copolymers (I) (Scheme 1) were dried at 0.1 Pa, at 35°C.

Number average molecular weights $(\overline{M}_n)$ were determined in toluene at 37°C with a Hewlett–Packard 502 high-speed membrane osmometer, $(\overline{M}_n)$ in the range of 30,000 to 75,000 g mol^{-1}.

The molar fraction of NVTBC units in the copolymer, α, was calculated from either the nitrogen content, obtained from elemental analysis, or the relative peak intensity of the methyl protons of the tert-butyl group in the ^{1}H-NMR spectrum. (Although the methylene peaks (a and b in Fig. 3) are fully separated, these peaks were nevertheless considered too small for proper analysis.)
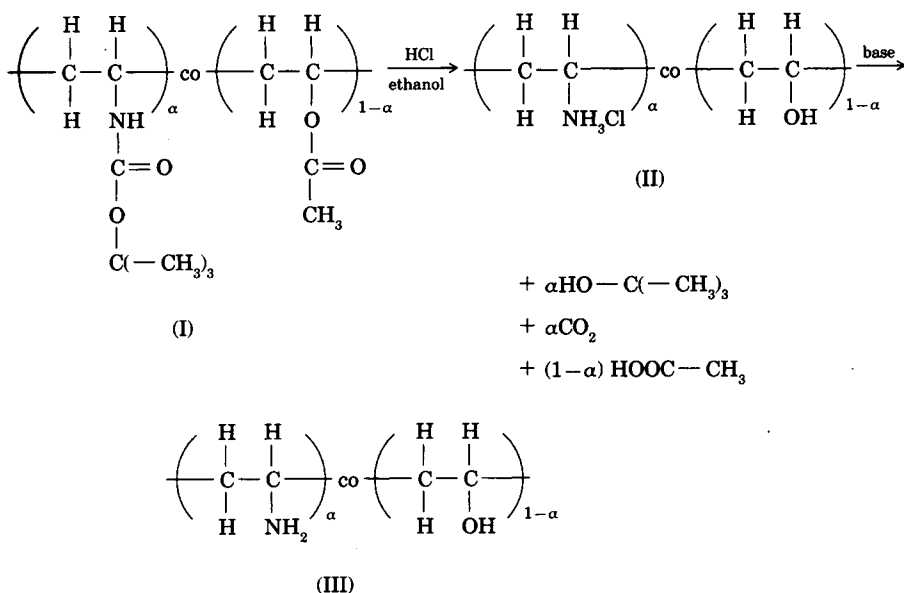
Scheme 1

Hydrolysis of Copolymers

Two grams of (I) were dissolved in absolute ethanol and added to a stirred 500-mL round-bottom flask by means of a dropping funnel. It was then mixed with an equal amount of concentrated HCl, added in the same manner, while the temperature was controlled not to exceed 30°C. The mixtures were stirred at room temperature for 48 h. From copolymers (II), with $\alpha > 70\%$ (type A), white, brittle precipitates were formed. From copolymers with α values in the range 0.5 to 0.7 (type B), white, clotty precipitates were obtained after a few hours of reaction, while from reaction mixtures containing copolymers with a lower value of α (type C), no precipitation was observed.

Isolation of Hydrolyzed Copolymers

Copolymers (II) of types A and B were isolated by filtration, washed with cold absolute ethanol, and dried under vacuum at room temperature. These products appeared to be very hygroscopic. Reaction mixtures containing copolymer (II) of type C were diluted with 100 mL of water, neutralized by hydrated sodium carbonate, and followed by removal of the alcohol fraction by rotary evaporation at 50°C. These solutions, mostly containing precipitated NaCl, were ultrafiltrated with distilled water (Diaflow Membrane YM-10, sharp cutoff: 10,000 MW) until no chloride could be detected in the eluent with a $AgNO_3/HNO_3$ test solution. It appeared that ultrafiltration was a safe and effective way of purification.

After eluting solutions of (II) through an Amberlite IRA 401 anion exchange resin in the OH^- form, solutions of deprotonated copolymers (III) were obtained. These copolymers were precipitated by pouring aqueous solutions of (III) into acetone.
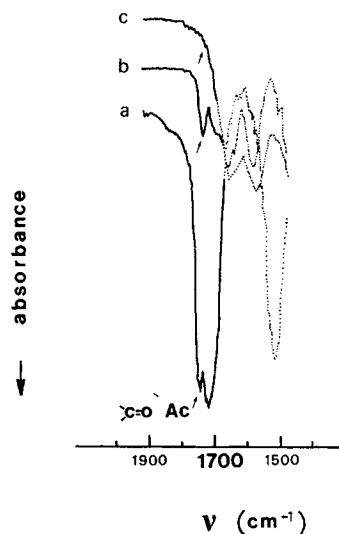
Fig. 1.   IR spectra of (I) ($\alpha = 0.56$) after hydrolysis during (a) 0 h, (b) 20 h, (c) 48 h. Arrows indicate the carbonyl group of the acetate moiety at 1750 cm^{-1}.

Analysis

Samples for IR spectra were prepared by evaporation of some drops of a methanolic solution of (III) on a KBr disk. Polymers (I) were dispersed in a KBr disk. Characteristic absorptions of (III) occurred at 3400 cm^{-1} (OH, NH$_2$), 2950 cm^{-1} (CH$_2$, CH), 1620 cm^{-1} (NH$_2$), 1470 cm^{-1} (CH$_2$, CH), 1100 cm^{-1} (CH), and 850 cm^{-1} (C–C).

Potentiometric titration of copolymers (III) was performed with HCl (0.03N) in the presence of 2M NaCl. Titration times were not shorter than 20 min, for reasons of reproducibility.

RESULTS AND DISCUSSION

Features of Synthesis

Complete hydrolysis of poly(N-vinyl-tert-butylcarbamate-co-vinylacetate) could be obtained after 48 h of reaction in a mixture of 1:1 v/v % ethanol/ concentrated HCl at room temperature. The hydrolysis of tert-butylcarbamate is completed within ½ h,[5] but the hydrolysis of the acetate is rather slow under these conditions. The rate of hydrolysis of the acetate group could be followed by monitoring the decrease in the –C=O band intensity at 1750 cm^{-1} in the IR spectra of the copolymers (Fig. 1). It is shown that after 20 h of reaction (b in Fig. 1) almost all VAc is hydrolyzed and after 48 h the reaction is complete.

Copolymers (II) were only soluble in water, but the deprotonated forms (III) were very soluble in both water and the lower alcohols in agreement with Nikolayev.[14]

Basicity of the Amine Groups

Copolymers (III) were subjected to potentiometric titration experiments with HCl in 2M NaCl. The results are shown in Figure 2, revealing that
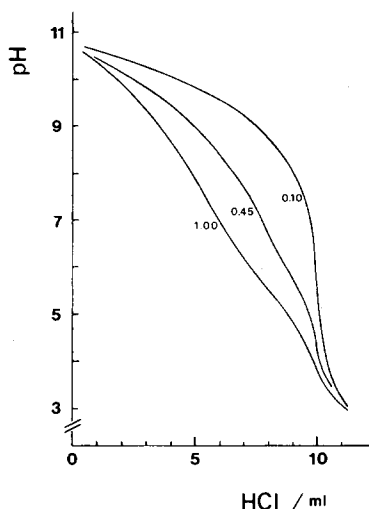
Fig. 2. Potentiometric titrations of copolymers (III) with 0.03N HCl in 2M NaCl. Solutions contain 0.3 mmol of amine groups. α values are given in the figure.

the individual amine groups possess a higher basicity as the amine group content in the copolymers is lower. This behaviour can be explained by assuming a decreased nearest neighbour interaction when the amine groups find themselves more isolated in the polymer chain at low values. On the grounds of these experimental observations, copolymers with a high degree of randomness or alternation are expected to be formed. In the following section this inference will be confirmed by measuring the copolymer reactivity ratios. The titration behaviour, shown in Figure 2, is in qualitative agreement with the titration experiments performed by Bloys van Treslong and Jansen[16] and by Kimura et al.[18] on copolymers (III) prepared according to the Hart method[5] and the Nikolayev method,[14] respectively.

Reactivity Ratios of NVTBC and VAc in Benzene

The dependence of copolymer composition on the monomer feed was evaluated for initial molar monomer feed ratios, q_0, in the range 0.05 to 4. Total conversion was mostly 15% but never exceeded 30%, to avoid large shifts in the monomer feed ratio.

Copolymer compositions were calculated from elemental analysis (C,H,N) of the purified, dried copolymers (I). For some of these copolymers the composition was determined from the methyl proton peak intensity of the tert-butyl group of (I) in the ^{1}H-NMR spectrum (shown in Fig. 3 for α = 0.43). In Table I values of α, obtained from NMR and elemental analysis data, are given, showing that within experimental error the NMR data are in good agreement with the elemental analysis results.

The reactivity ratios of monomers (1) and (2) have been evaluated according to the methods of Fineman and Ross[19] and Kelen and Tüdős.[20] These methods were selected on the grounds of experimental convenience, since in the present case copolymer compositional analysis data appeared to be available much more easily and accurately than monomer feed data during the polymerization.

In the Fineman–Ross method the parameters $F = (\overline{q})^2/x$ and $G = \overline{q}(x -$
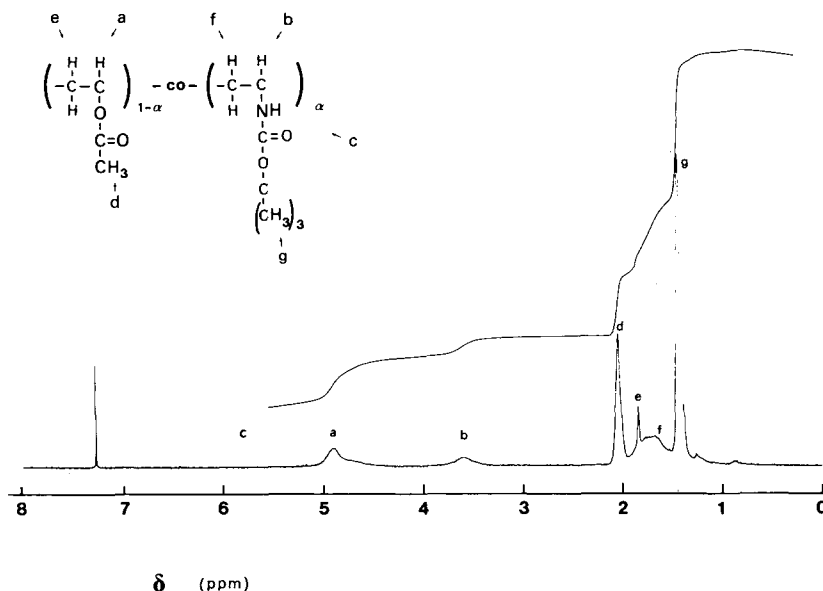
$$\delta \quad (ppm)$$

Fig. 3. ^{1}H-NMR spectrum of (I) ($\alpha = 0.43$) in CDCl$_3$ with CHCl$_3$ as internal standard. Peaks correspond to the hydrogen atoms indicated.

1)/x are evaluated, where $\bar{q}$ = the average ratio of molar concentrations of monomers (1) and (2) and x = the molar ratio of these monomers in the copolymers. This analysis is shown in Figure 4. In the calculations, q_0 instead of $\bar{q}$ was used, since simulation experiments[21] show that for the present pair of r values and degree of conversion any possible deviations of these r values, introduced by substituting q_0 for $\bar{q}$, will be within the error intervals given for the Fineman–Ross method. Moreover, in Figure 4
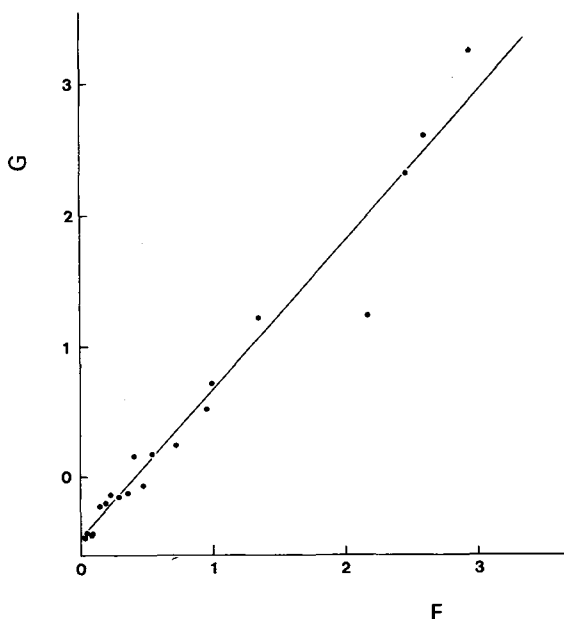

Fig. 4. Fineman–Ross plot; the intercept gives $-r_2$ and the slope gives r_1.
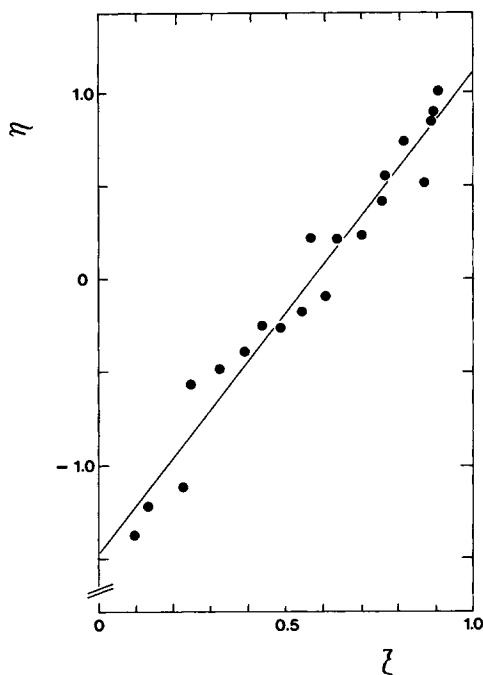
Fig. 5.   Kelen–Tüdös plot; the intercept at $\xi = 0$ gives $-r_2/\beta$, and the intercept at $\xi = 1$ gives r_1. $\beta = 0.31$.

the experimental points derived from relatively high conversion (30%) experiments do not deviate significantly more from the drawn linear fit than do the points pertaining to lower conversion experiments. In the method designed by Kelen and Tüdös for low conversion, the experimental points are symmetrized by introducing the parameter $\beta = (F_{min}F_{max})^{1/2}$ in the dependent variables $\xi = F(\beta + F)$ and $\eta = G(\beta + F)$. According to the latter method, data contained in Figure 4 were replotted in Figure 5. Reactivity ratios calculated from Figures 4 and 5 are given in Table II, which shows that the results of both methods are in good agreement. Obviously, the effect on r_1 and r_2 of symmetrization of the experimental points as occurs in the Kelen–Tüdös method is negligible. The values of r_1 and r_2 found here (1.14 $\pm$ 0.05 and 0.47 $\pm$ 0.05, respectively) deviate considerably from the values recently reported by Bloys van Treslong and Jansen,[16] viz., 1.8 $\pm$ 0.2 and 0.76 $\pm$ 0.11, respectively.

TABLE I

Comparison of Copolymer Compositional Determination by Elemental Analysis (C,H,N) and ¹H-NMR

Mole fraction of NVTBC in monomer feed	α^a (CHN)	α^b (¹H-NMR)
0.80	0.84 $\pm$ 0.05	0.83 $\pm$ 0.06
0.59	0.67 $\pm$ 0.04	0.74 $\pm$ 0.05
0.31	0.43 $\pm$ 0.03	0.44 $\pm$ 0.03
0.18	0.33 $\pm$ 0.02	0.30 $\pm$ 0.02
0.13	0.20 $\pm$ 0.01	0.21 $\pm$ 0.02

[a] Nitrogen content of (I) has been used.
[b] Methyl proton peak intensity of the tert-butyl group in (I) has been used.

TABLE II
Reactivity Ratios of NVTBC and VAc in Benzene, Calculated According to the Methods of
Fineman and Ross (F–R) and Kelen and Tüdös (K–T)

Method of data analysis	r_1	r_2
F–R	1.14 ± 0.05	0.47 ± 0.07
K–T	1.12 ± 0.07	0.46 ± 0.03

However, their experimental points do not seriously conflict with ours as would appear from plotting their data in Figure 4. The main reason for the discrepancy in the reactivity ratio values is that although the latter authors used a calculation method essentially the same as the Fineman–Ross procedure[19] only a few experimental points within a very narrow range of monomer feed ratios were available, not enough for determining the reactivity ratios sufficiently accurately.

Summarizing, more accurate reactivity ratios will be obtained when using more experimental data obtained from copolymerization experiments over a wider range of monomer feed compositions. If possible, the copolymer compositional analysis should be confirmed by a second technique. On these grounds, we believe our present data to be the more reliable.

Sequence Distribution

The distribution of monomer units in the copolymer is directly related to the reactivity ratios, the latter being measures of the probability of occurrence of homogeneous sequences of either monomer unit. To gain insight into the randomness of the monomer unit distribution along the polymer chain, the relative numbers of amine–amine, amine–alcohol, and alcohol–alcohol neighbouring groups as well as the number average sequence length of either monomer have been calculated[22] and compared with a situation of Bernouillian distributed, i.e., purely randomly, sequenced monomer units. In Table III the results are listed for a copolymer with α = 0.43. A more sensitive indicator of deviations from the Bernouillian distribution is the so-called monomer dispersity index, MD, which is defined as $100/\bar{l}$, where $\bar{l}$ is the number average sequence length.[23] An MD value

TABLE III
Calculated Diad Abundance and Number Average Sequence Length in One of the Present
Copolymers as Compared with a Hypothetical Bernouillian-Type Copolymer (α = 0.43)

		Present copolymer[a]	Perfectly Bernouillian sequenced copolymer
	11	15	18
Diad abundance (%)[b]	12 + 21	57	49
	22	29	32
Sequence length[b]	$\bar{l}_1$	1.51	1.75
	$\bar{l}_2$	2.00	2.33

[a] $r_1 = 1.12$, $r_2 = 0.46$, $q_0 = 0.46$.
[b] 1 = Vinylamine unit, 2 = vinylalcohol unit.
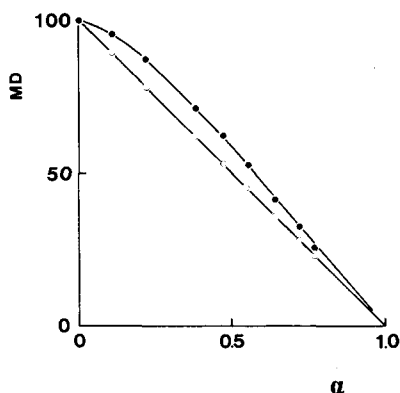
Fig. 6. Monomer dispersity of vinylamine units versus α. ($\bullet$) In the presently synthesized copolymers, ($\bigcirc$) in hypothetical Bernouillian-type copolymers.

of 100 would indicate that all vinylamine units occur isolated in alcohol–amine–alcohol sequences. Any value below 100 is indicative of the occurrence of contiguous amine–amine units.

In Figure 6, values of MD of vinylamine units for copolymers formed according to the present pair of r values as well as for a hypothetical perfect Bernouillian-type copolymer are plotted versus the copolymer composition α. From the calculations (Table III and Fig. 6) it may be concluded that in the reaction of NVTBC with VAc random copolymers are formed with a slight tendency toward alternation. These copolymers are therefore eminently suitable as polymeric ligands in a study on the relation between base density within a polymeric thiol oxidation catalyst and catalytic activity. The results of this study will be reported separately.

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