Polymer Bulletin 23, 13–18 (1990)

**Polymer Bulletin**

# Radical copolymerization of N-vinyl-t-butylcarbamate

## Preparation of vinylamine copolymers

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## SUMMARY

The radical copolymerization of N-vinyl-tert-butylcarbamate (NVTBC) with styrene, methyl methacrylate, vinyl-pyrrolidone and 4-vinyl-pyridine was studied at 50-60° C in toluene, methanol or dioxane, using azo- bis- isobutyronitrile as the initiator. The reactivity ratios of the monomers were calculated from monomer feed and copolymers composition data using the Fineman-Ross method.

The copolymers were hydrolysed in $CH_3COOH$/ HCl mixtures at room temperature in order to obtain vinylamine containing copolymers. The extent of the solvolysis is dependent on the nature of the comonomer.

The solvolysed copolymers bearing $NH_2$ groups were titrated by HCl in 2M NaCl medium in order to have more informations on the repartition of the NVTBC residues.

## INTRODUCTION

Polymeric amines and especially polymers containing vinyl amine have received increasing attention during last years. These polymers present important features such as water solubility, high basicity of the amine group and complexation properties toward metal ions.

The copolymerization of vinylamine with other monomers seems of interest but, at our knowledge, only few of these copolymers have been reported. Vinylamine-sodium vinylsulfonate copolymers have been prepared by hydrolysis of copolymers of N-vinylacetamide and sodium vinylsulfonate (1) More recently, copolymers of vinylamine and vinylalcohol were obtained from copolymers of hydrolysis of N-vinyl tert-butylcarbamate (NVTBC) and N-vinylacetate (2,3). In these cases, the reactivity ratios of the pre-monomers were determined. In earlier works, the same copolymer was prepared from N-vinyl phtalimide and N-vinyl acetate, but the rectivity ratios were not given (4,5).

In a previous work, we have described the synthesis of macroporous copolymers containing vinylamine, using a suspension polymerization process in the presence of a porogenous agent (6). It was shown that the amount of the vinylamine residue in the beads depends on the

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*To whom offprint requests should be sent nature of the comonomer, the nature of the crosslinking agent (divinylbenzene, DVB or ethylene glycol dimethacrylate, DMG) and of the extent of transformation of the NVTBC residue into vinylamine (solvolysis).

Thus, it seemed necessary to investigate the linear copolymerization of NVTBC with styrene and methylmethacrylate (MMA) (considered as an homolog of DMG) and the solvolysis of the resulting copolymers. Copolymers with vinylpyrrolidone(VP) and 4-vinyl pyridine(4-VP) were also studied.

## EXPERIMENTAL

### Materials

The N-vinyl-tert butylcarbamate (NVTBC) was synthesized according to the Hart method (7) and characterized by I.R. spectroscopy. Other monomers were commercial products and were distilled under reduced pressure before use.

The initiator, azo-bis-isobutyronitrile (AIBN) was used as received.

### Polymerization

The copolymerizations were carried out in sealed tubes with an initiator concentration of 1%. The monomer mixtures were degassed by cycles of freezing, pumping off and thawing.

As both monomers must be soluble in the polymerization medium, the temperature and solvent of copolymerization were dependent on the nature of the monomers: 60°C in toluene for NVTBC-styrene, 50°C in methanol for NVTBC-MMA, 60°C in dioxane for NVTBC-VP and 50°C in methanol for NVTBC-4-VP.

The copolymers were isolated by precipitating the reaction mixture in a large excess of hexane. After drying, the samples were characterized by their I.R. spectra using the bands at 3400 $cm^{-1}$(N-H) for NVTBC, 3000-3100 $cm^{-1}$(aromatic C-H) for styrene, 1240-1160 $cm^{-1}$(C-O) for MMA, 1290 $cm^{-1}$(C-N) for VP and 1600 $cm^{-1}$(C=N) for 4-VP.

The molar fraction of NVTBC units in the copolymers was calculated from the nitrogen and oxygen content obtained by elemental analysis.

### Hydrolysis of the copolymers

The copolymers were dissolved in acetic acid and added dropwise to a 20-fold excess of concentrated chlorhydric acid. The mixture was stirred during 6 hours at room temperature. The hydrolysed copolymers were recovered by precipitation in acetone, ethanol or ethyl acetate. Vinylamine- vinylpyrrolidone samples are highly hygroscopic.

### Potentiometric titrations

Copolymers obtained from solvolysis are under the $NH_3^+ Cl^-$ form. For the purpose of potentiometric titrations, they were converted into the $NH_2$ form by use of an anion exchange resin.

Solutions containing about 0.3 mmole of $NH_3^+$ $Cl^-$ groups were mixed with 5 g of Amberlite IRA 401 and allowed to stir during 24 h. After filtration, the resulting solutions were titrated with 0.03 N HCl in the presence of 2 M NaCl. The solutions were somewhat cloudy but became clearer and more viscous upon titration.

## RESULTS AND DISCUSSION

### Yield of copolymerization

The copolymerization of NVTBC-MMA in methanol and of NVTBC-VP in dioxane led to high degrees of conversion within 24 h (60-85%). On the contrary, in the copolymerization of NVTBC with styrene or 4-VP, the yield never exceed 20% even after 40 h.

### Reactivity ratios

The dependence of copolymer composition on the monomer feed was evaluated for NVTBC composition $f_a$ ranging between 0.1 and 0.95 and for the determination of the reactivity ratios, the conversion was kept rather low.

Fig.1 shows the dependence of the copolymer composition in NVTBC, $F_a$ versus $f_a$. When using styrene as comonomer, the incorporation of NVTBC is very low. With MMA, the amount of NVTBC in the copolymer is higher but $F_a$ is always lower than $f_a$. On the contrary, VP-NVTBC copolymers contain high amounts of NVTBC. Upon transformation of the NVTBC residues into vinylamine groups, it is thus possible to obtain water-soluble copolymers containing a high density of functional groups.

Copolymers with 4-VP were gummy, colored and thus suspected to have undergo some chemical transformation during polymerization or precipitation. For this reason, they were not further studied though they contained high amounts of NVTBC ($F_a$=0.5 for $f_a$=0.5).

The reactivity ratios $r_1$ and $r_2$ of monomers (1) (NVTBC) and (2) (comonomer) have been evaluated according to the method of Fineman and Ross (8). This calculation was made only on the NVTBC-MMA and NVTBC-VP systems and the values are given in Table 1. In the case of NVTBC-Styrene, the incorporation of NVTBC was too low to allow precise measurement.

Fig.2 gives the results obtained for the suspension polymerization of NVTBC with styrene in the presence of divinylbenzene (DVB) or ethyleneglycol dimethacrylate (DMG) as cross-linking agent (6). In the case of DVB, the incorporation of NVTBC is low and this can be explained by a comparison with the corresponding linear copolymerization (Curves 1 of Figs.1 and 2). Nevertheless, the replacement of styrene by DVB facilitates the incorporation of NVTBC. The replacement of styrene by MMA (curves 1 and 2 in Fig.1) also increases the incorporation of NVTBC and this could explain the results obtained with DMG instead of DVB as a cross-linking agent in Fig.2, if we assume that DMG can be considered is an analog of MMA on the basis of their chemical composition.

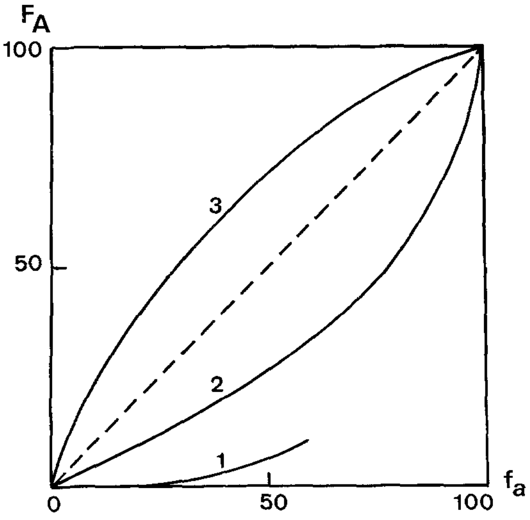

Fig.1 Copolymer composition versus monomer feed composition for the linear copolymerization of NVTBC with: (1) styrene; (2) MMA ; (3) VP

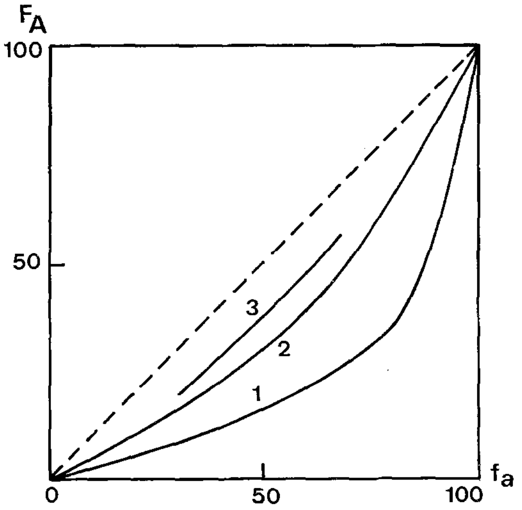

Fig.2 Weight fraction of NVTBC in the cross-linked copolymer vs the weight fraction in the feed: (1) NVTBC-styrene-DVB;(2) NVTBC-styrene-DMG;(3) NVTBC-MMA-DMG

| Monomers | r1 | r2 |
|---|---|---|
| NVTBC-MMA | 0.17 +- 0.10 | 1.87 +- 0.2 |
| NVTBC-VP | 2.4 +- 0.5 | 0.4 +- 0.06 |

Table 1 - Monomer reactivity ratios of NVTBC with methylmethacrylate and vinylpyrrolidone.

### Yield of solvolysis

The extent of the transformation of the NVTBC groups into $NH_3^+ Cl^-$ (VA) groups was nearly complete for the NVTBC-MMA samples ( over 90% ). For the NVTBC-VP series, the yield of solvolysis was about 60%. In this case terpolymers were obtained.

### Potentiometric titrations

The copolymers were subjected to potentiometric titration experiments with HCl in 2M NaCl. In these conditions the long range electrostatic interactions are screened by the high concentration of added salt and only short range interactions between neighbouring groups are reflected in the shape of the titration curves.

Fig.3 shows the variation of pH with the degree of neutralization a of the $NH_2$ units. Comparison of curves (1)-(4) shows the progressive effect of electrostatic interactions. For sample (1) in which the amine content is low, the individual amine groups possess a high basicity and the titration curve looks like that of a small molecule. The $r_1$ value for this series indicates that sequences of amine groups are not likely. When increasing the amount of vinylamine, nearest neighbourg interactions increase and the amino groups seem to be less basic i.e. at constant a value, the apparent pK and the pH decrease down to pure poly(vinylamine) (4).

The comparison of curves (2) and (5) is interesting. The two samples have about the same content of $NH_2$ groups (40%). Nevertheless, the behaviour of sample (5) is closer to that of samples (3) or (4) which have a higher $NH_2$ content than that of sample (2). This is not due to the nature of the comonomer since the replacement of MMA by VP, which is more hydrophilic and has a higher dielectric constant, should have the opposite effect. The value of $r_1$=2.4 for NVTBC in NVTBC-VP copolymers indicates that rather long sequences of NVTBC and thus of VA residues is likely to occur and can explain the results of potentiometric titrations.

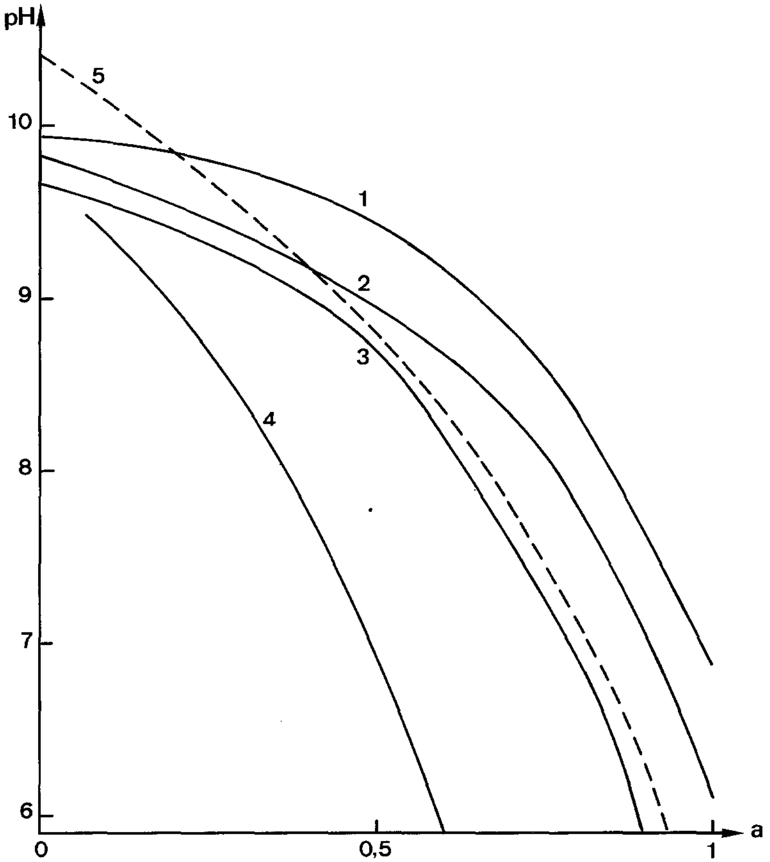

Fig.3 Titration curves of: Vinylamine-MMA copolymers: mole fraction of $NH_2$ groups: (1) 0.28; (2) 0.36; (3) 0.67; (4) 1 . (5) Vinylamine-VP copolymer with 0.42 mole fraction of $NH_2$

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Accepted November 14, 1989 C