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Radiation-Induced Copolymerization of N-Vinylpyrrolidone with Monochlorotrifluoroethylene

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ABSTRACT

The copolymerization of N-vinylpyrrolidone (NVP) with chlorotrifluoroethylene (CTFE), initiated by gamma rays from a ^{60}Co source, has been studied at temperatures of 20 to -78°C in a dose rate range of 5×10^4 to 3.8×10^5 rd/h. The copolymerization rate was proportional to the 0.5 power of dose rate and showed a maximum at the equimolar concentration of both monomers. The apparent overall activation energy of copolymerization was determined to be 5.8 kcal/mol. 1,1-Diphenyl-2-picrylhydrazil was found to be a strong inhibitor. The composition curve indicated a strong alternating copolymerization tendency. The monomer reactivity ratios were determined to be $r(\text{NVP}) = 0.38$ and $r(\text{CTFE}) = 0.30$, respectively, by the Fineman-Ross method. The copolymer obtained is a white powder. It is soluble in such solvents as acetone, dimethylformamide, and chloroform, but insoluble in water.

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INTRODUCTION

It is well known that N-vinylpyrrolidone (NVP) is polymerized readily by such free radical initiators as α, α' -azobisisobutyronitrile (AIBN) and hydrogen peroxide [1, 2]. The homopolymer of NVP (PNVP) has been used for adhesives, cosmetics, detergents, and pharmaceuticals [3-5]. PNVP was used extensively as a blood plasma extender during World War II.

NVP polymerization has been studied by many researchers. The radiation-induced graft copolymerization of NVP onto PTFE and the copolymerization of NVP with trifluorostyrene have been carried out for the purpose of developing new cation-exchange membranes with good physical and chemical properties [6, 7].

In the present work, NVP was used as a hydrophilic monomer and copolymerized with hydrophobic monomer to obtain new materials such as ion-exchange membranes or biomaterials. Monochlorotrifluoroethylene (CTFE) was selected as the hydrophobic comonomer because of its good physical and chemical properties.

This paper mainly describes a kinetic study of the copolymerization.

EXPERIMENTAL

CTFE, purchased from PCR Research Chemicals, was used after vacuum distillation. NVP was distilled under reduced pressure (15 mmHg at 97-98°C). Reagent grade chloroform was used as the solvent.

Pipetted amounts of NVP and CHCl_3 were introduced into a 10-cm³ glass ampule. The ampule was connected to a vacuum system and immersed in liquid nitrogen. A certain amount of CTFE was introduced into the frozen ampule through the vacuum system, and then the ampule was evacuated to 10⁴ torr after solidification of the monomers. The entrapped trace amounts of oxygen in the ampule were purged by the freeze-thaw technique.

After irradiation, unreacted monomer and solvent were expelled from the reactant mixture under reduced pressure at room temperature. The dried product was dissolved in acetone, and excess water was added to it. The precipitated copolymer was collected on filter paper and then washed and dried under vacuum at room temperature.

The structure of the copolymer was investigated by means of infrared spectroscopy. The composition of the copolymer was determined from elemental analysis of the fluorine atom.

RESULTS AND DISCUSSION

Polymerization proceeded in a homogeneous liquid phase, and the white powder product was obtained.

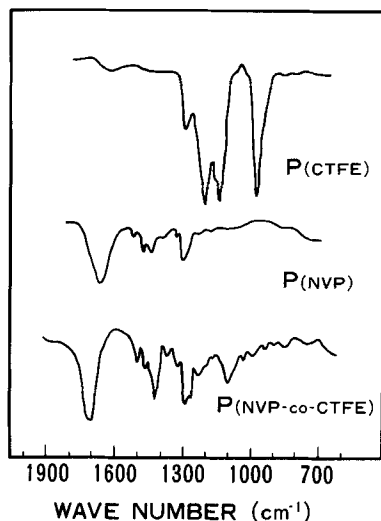


FIG. 1. Infrared spectra of polymers obtained at constant conditions: Dose rate, 3.8×10^5 rd/h; polymerization temperature, 20°C ; molar ratio of NVP in monomer mixture, $[\text{NVP}]/[\text{CTFE}] = 1.0$.

The infrared spectra of the product and of each homopolymer are shown in Fig. 1. The spectrum of product has two absorption peaks which are ascribed to both the $-\text{CF}$ stretching vibration of polychlorotrifluoroethylene (PCTFE) and the $-\text{CN}$ stretching vibration of poly-N-vinylpyrrolidone (PNVP). The peaks are at 1100 and 1710 cm^{-1} , respectively. This suggests that the product is a copolymer of NVP with CTFE.

Other experimental results, such as solubility test and elemental analysis, also showed that the product obtained is a copolymer (described later). Therefore, on the basis of these results, we conclude that NVP is copolymerized with CTFE.

Figure 2 shows the relation between conversion and irradiation time. The conversion increases linearly with irradiation time up to about 70%.

The dependences of the copolymerization rate on both temperature and dose rate are shown in Figs. 3 and 4. As is obvious from Fig. 4, the rate of copolymerization is proportional to the 0.5 power of the dose rate, indicating that termination proceeds mainly via bimolecular reactions. From Fig. 4 the apparent activation energy of copolymerization is 5.8 kcal/mol . These dose rate and temperature dependences suggest that copolymerization occurs via a radical mechanism.

In fact, the copolymerization was found to be inhibited by 1,1-diphenyl-2-picrylhydrazil (DPPH) which is a radical scavenger.

The copolymerization rate as a function of the molar ratio of both

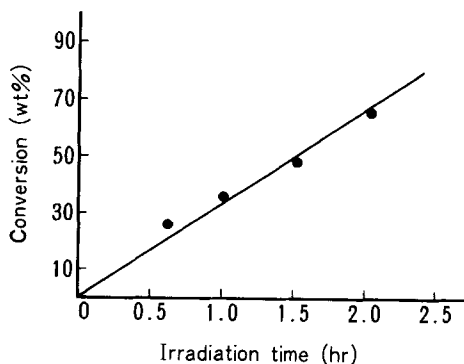


FIG. 2. Time-conversion plot. Dose rate, 3.8×10^5 rd/h; polymerization temperature, 20°C ; molar ratio of NVP in monomer mixture, $[\text{NVP}]/[\text{CTFE}] = 1.0$.

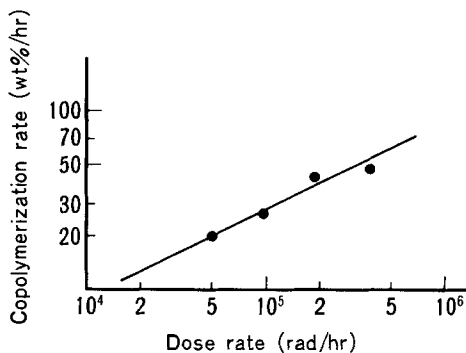


FIG. 3. Dose rate dependency of the copolymerization rate. Polymerization temperature, 20°C ; molar ratio of NVP in monomer mixture, $[\text{NVP}]/[\text{CTFE}] = 1.0$.

monomers is shown in Fig. 5, and the composition curve is shown in Fig. 6. From these two figures the structure of the copolymer can be said to be of an alternative nature because 1) a maximum copolymerization rate is attained by about 50 mol% CTFE in the monomer mixture; and 2) reactivity ratios of both monomers are $r(\text{NVP}) = 0.38$ and $r(\text{CTFE}) = 0.30$ as determined by the Fineman-Ross method [8], and the product of both reactivity ratios ($r(\text{NVP}) \times r(\text{CTFE})$) is below 1.

The results of the solubility test of the copolymer are shown in Table 1. The difference in solubility between the copolymer and each homopolymer is obvious. That is, the copolymer is soluble in THF while both homopolymers are insoluble in THF.

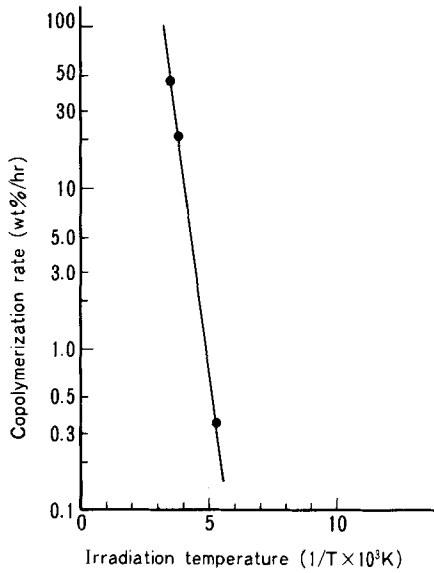


FIG. 4. Arrhenius plot. Dose rate, 0.8×10^5 rd/h; molar ratio of NVP in monomer mixture, $[NVP]/[CTFE] = 1.0$

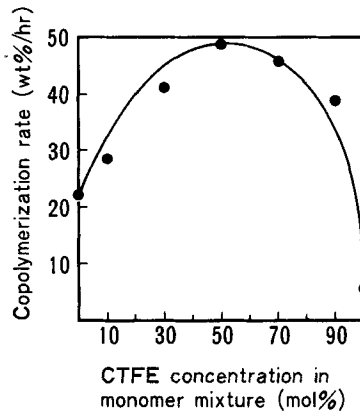


FIG. 5. Relation between CTFE concentration in monomer mixture and copolymerization rate. Dose rate, 3.8×10^5 rd/h; polymerization temperature, 20°C .

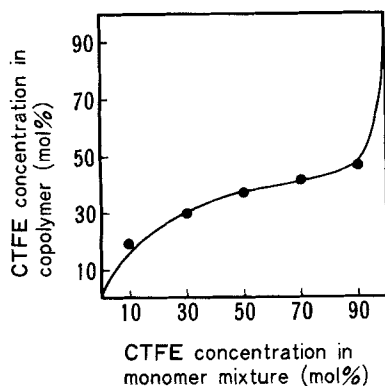


FIG. 6. Composition curve derived from elemental analyses of fluorine.

TABLE 1.^a Solubility Test of PNVP, PCTFE, and P(NVP-co-CTFE)

Solvent	Solubility		
	PNVP	PCTFE	P(NVP-co-CTFE)
H ₂ O	O	X	X
Acetone	O	X	X
CHCl ₃	O	X	X
Toluene	X	X	X
DMF	O	X	O
THF	X	X	O
CCl ₄	X	X	X
CH ₃ OH	O	X	O

^aO, soluble; X, insoluble. These tests were carried out at room temperature. P(NVP-co-CTFE) was obtained at the following constant conditions: Dose rate, 3.8×10^5 rd/h; polymerization temperature, 20°C; molar ratio of NVP in monomer mixture, $[NVP]/[CTFE] = 1.0$.

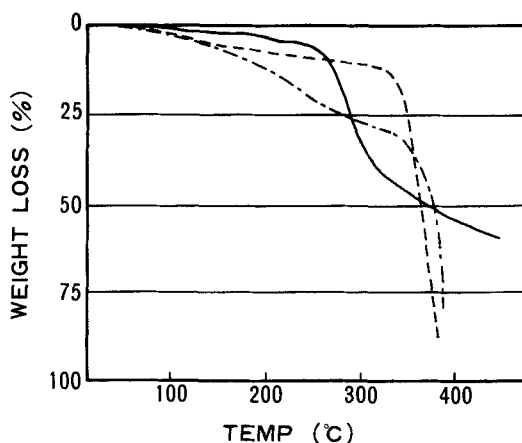


FIG. 7. Thermogravimetric analysis of PCTFE (---), PNCP (-.-), P(NVP-co-CTFE) (—) (50 mol% NVP in monomer mixture).

The thermal resistance of the copolymer was examined by using a thermal analyzer. Figure 7 exhibits the TG curves of PNVP, PCTFE, and P(NVP-co-CTFE). The curves indicate that the thermal resistance of PNVP is improved by copolymerization with CTFE.

The molecular weight of P(NVP-co-CTFE) was roughly estimated by the GPC method. By reference to a calibration curve of standard polystyrene samples, the molecular weight was found to be below 10,000.

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