

Synthesis and properties of perfluorocarboxylated polymers

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Abstract

Copolymerization of tetrafluoroethylene and perfluorovinyl ether having carboxylated group in the side chain was investigated. A series of new perfluorocarboxylated polymers with various functional group contents were synthesized by radical polymerization procedure and their structures were examined by IR, NMR spectrometry, osmometry, and X-ray diffraction analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tetrafluoroethylene; Perfluorovinyl ether; Perfluorocarboxylated polymer

1. Introduction

Perfluorinated ion exchange membranes have received much attention both industrially and academically in recent years. Particularly, the adoption of them in the chlor-alkali process has been proving a considerable growth area. Such membranes are based upon perfluorinated polymers having either carboxyl or sulfonyl group as the functional group. Perfluorinated sulfonic acid polymers were first made in the early 1970s [1]. Although they were originally developed for the use as a solid polymer electrolyte in the fuel cell, the application to the chlor-alkali process was studied worldwide. As the development proceeded, perfluorosulfonic acid polymers were found not to show sufficient performance. This was considered to be resulted from high water affinity of the polymers due to the presence of the strongly acidic sulfonic group. Thus, perfluorocarboxylic acid polymers were investigated in order to improve the permselectivity. This paper deals with the synthesis of such perfluorocarboxylic acid polymers.

2. Experimental detail

2.1. Monomer synthesis

Perfluorocarboxylated vinyl ethers such as methyl perfluoro-5-oxa-6-heptenoates, methyl perfluoro-6-oxa-7-octenoate, and methyl perfluoro-5,8-dioxa-6-methyl-9-decenoate were synthesized as previously reported [1].

2.2. Polymerization

Copolymerization of tetrafluoroethylene and functional vinyl ethers was carried out in solution, bulk or emulsion system using a radical initiator. Required amounts of functional monomer, initiator, and additives were charged into a 0.2 l stainless steel autoclave. After degassing, the reactor was heated to a definite temperature and then tetrafluoroethylene was fed into the reactor. During the polymerization, tetrafluoroethylene was introduced continuously to keep the reaction pressure constant. After the polymerization, copolymers were recovered by filtration, washed successively with 1,1,2-trichloro-1,2,2-trifluoroethane, and dried.

3. Results and discussion

3.1. Preparation of polymers

Perfluorocarboxylated polymers which we newly synthesized have general formulae as shown in Fig. 1. These polymers are copolymers of tetrafluoroethylene and perfluorovinyl ether having a carboxylated group instead of a sulfonated group. Typical functional monomers were methyl perfluoro-5-oxa-6-heptenoate, methyl perfluoro-6-oxa-7-octenoate, and methyl perfluoro-5,8-dioxa-6-methyl-9-decenoate. Hereinafter, these monomers are referred to as M_1 , M_2 and M_3 , respectively.

The molar ratio of functional perfluorovinyl ether to tetrafluoroethylene in copolymer is directly related to ion exchange capacity of the resulting polymeric acid. This ratio

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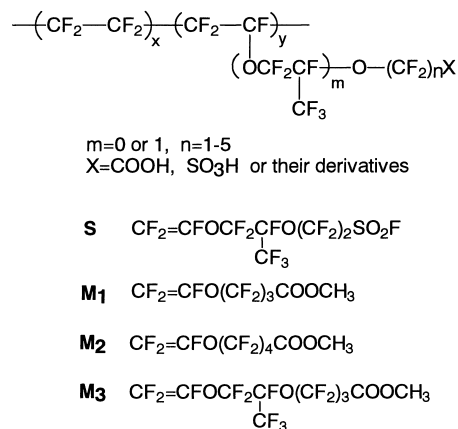


Fig. 1.

can be controlled by monomer feed ratio in the copolymerization procedure. Since perfluorovinyl ethers have been known to be radically active, copolymerization of tetrafluoroethylene and functional perfluorovinyl ether was carried out by using a radical initiator. Fig. 2 shows a typical time-conversion curve in the copolymerization of tetrafluoroethylene and **M₁** by bulk system using azobisisobutyronitrile as an initiator. As shown in the Fig. 2, the reaction started without appreciable induction period. The yield of copolymer increased linearly with reaction time and the copolymer composition did not change during the polymerization in a wide range of the polymer concentration. Fig. 3 shows the dependence of copolymer composition upon the reaction pressure of tetrafluoroethylene.

The content of functional monomers in the copolymer increased with the decrease of reaction pressure of tetrafluoroethylene. Thus, copolymers having various vinyl ether contents were obtained with good reproducibility by regulating the reaction pressure precisely. Fig. 4 shows the copolymer composition curve obtained for the copolymerization of tetrafluoroethylene and functional monomers (**M₁**

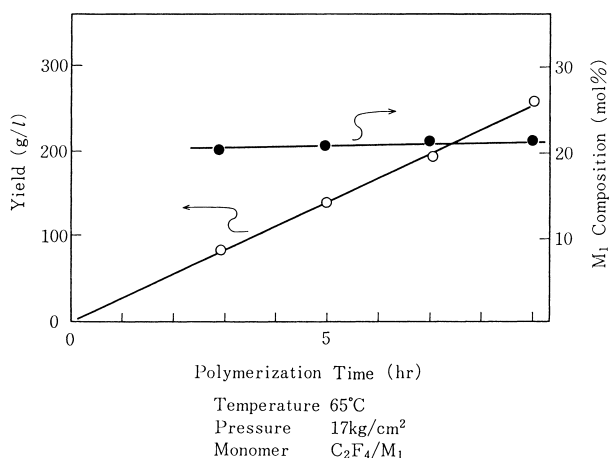
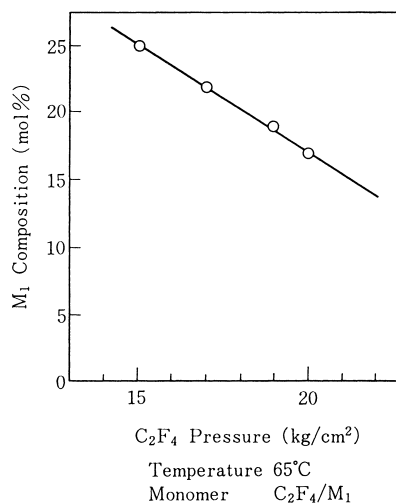


Fig. 2. Time-conversion of polymerization.

Fig. 3. Dependence of copolymer composition upon C_2F_4 pressure.

and **M₃**). The curve in this figure clearly indicates that both monomers have almost the same reactivity toward tetrafluoroethylene irrespective of the difference of side chain length. The monomer reactivity ratios of tetrafluoroethylene and functional vinyl ethers were calculated as 7.0 and 0.14, respectively, by using Fineman-Ross method. From these reactivity ratios, Q and e values of each monomer were derived by the Alfrey-Price equation. Since Q and e values of tetrafluoroethylene are known to be 0.049 and 1.22, Q and e values of functional vinyl ethers were obtained as 0.0057 and 1.08, respectively. The much smaller Q value of these vinyl ethers as compared with that of tetrafluoroethylene explains their lower reactivity than that of tetrafluoroethylene. Monomer reactivity ratios of tetrafluoroethylene and perfluorosulfonated vinyl ether are also reported to be 8.0 and 0.08 [2,3]. These data indicated that functional vinyl ethers with carboxylated and sulfonated groups have nearly the same reactivity toward tetrafluoroethylene.

3.2. Characterization

Characterization of polymers were carried out mainly with copolymers of tetrafluoroethylene and **M₁**. Fig. 5 shows a typical IR spectrum. The absorption at 2960 and 1780 cm^{-1} is due to carbon-hydrogen bond and carbonyl bond in ester group, respectively. The absorption in the range of $1100\text{--}1300\text{ cm}^{-1}$ is assigned to carbon-fluorine bonds, which appear commonly in fluorocarbon polymers. The formation of copolymers were also confirmed by fluorine NMR spectrum giving their characteristic peaks as shown in Fig. 6.

Whereas methyl ester type copolymers were insoluble in common solvents, decyl ester type copolymers were soluble in fluorine-containing solvents such as chlorobenzotrifluoride. Thus, molecular weight of copolymers were measured by using an osmotic pressure method and found to be in the range of $10^5\text{--}10^6$. In Fig. 7, molecular weight is plotted

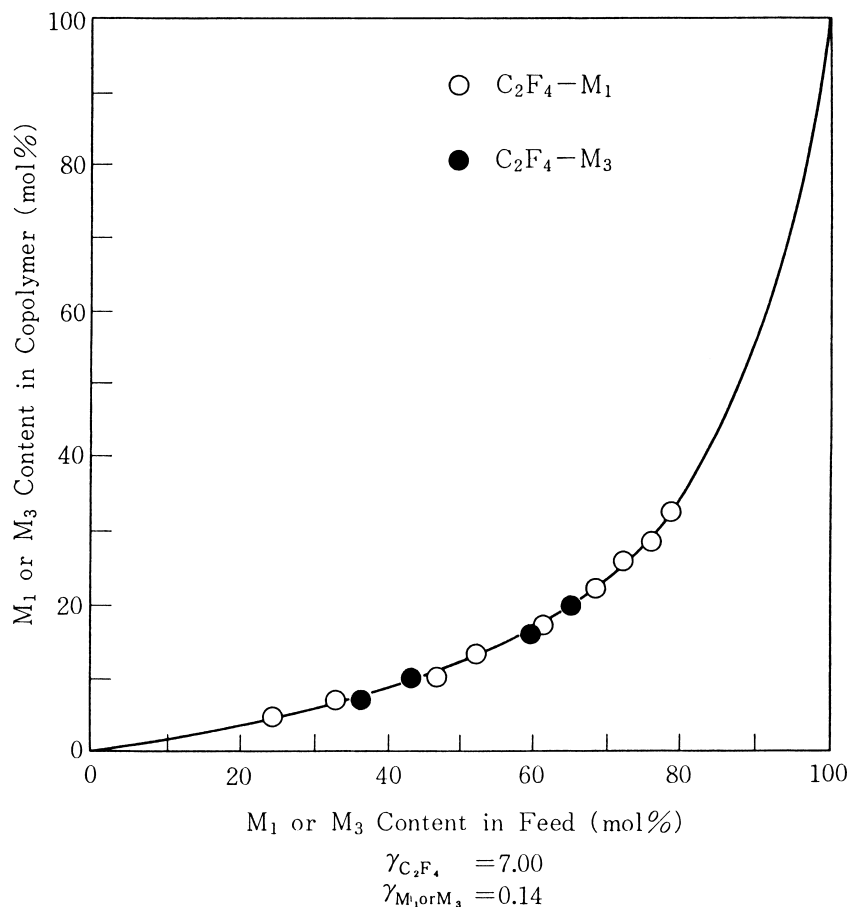


Fig. 4. Copolymer composition curve.

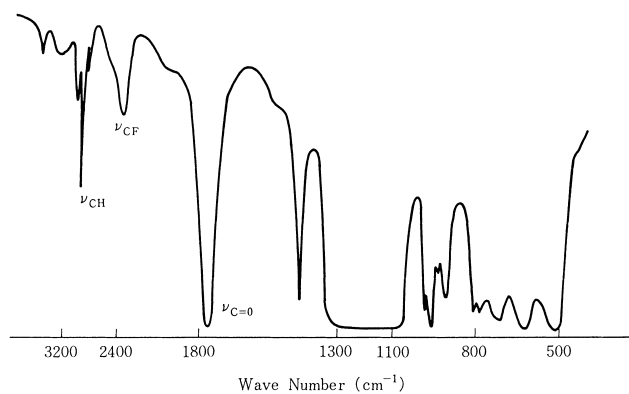
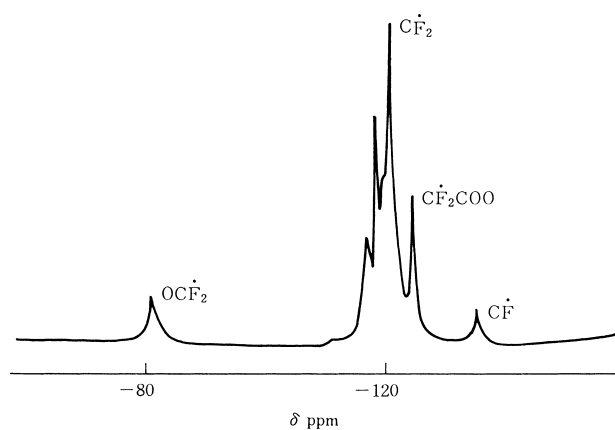


Fig. 5. IR spectrum of copolymer.

Fig. 6. ^{19}F NMR spectrum of copolymer.

against T_Q value which is defined as the temperature at which the volumetric melt flow rate of copolymer is $100 \text{ mm}^3/\text{s}$ through the orifice of 1 mm diameter and 1 mm length under the load of $30 \text{ kg}/\text{cm}^2$. As shown in this figure, logarithmic molecular weight has a good linear relationship with T_Q value. Crystallinity of copolymers was measured by the wide angle X-ray diffraction method

as in Fig. 8. It decreased with increasing functional vinyl ether content and the copolymer became almost amorphous above the vinyl ether content of 20 mol %.

Furthermore, copolymers were melt processable as shown in Fig. 9. Properties of the polymers, such as tensile property, ion permselectivity, and conductivity will be reported elsewhere.

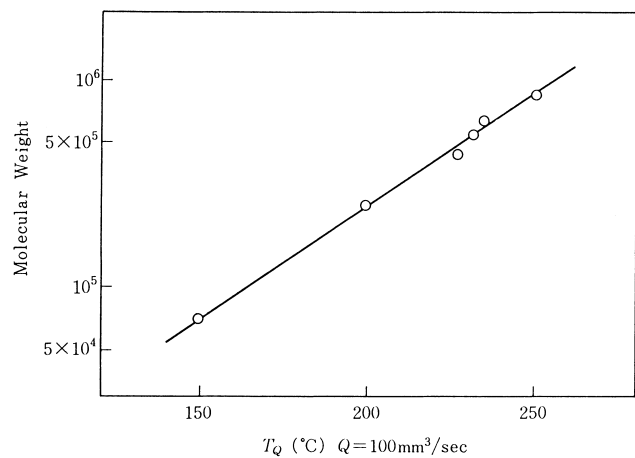
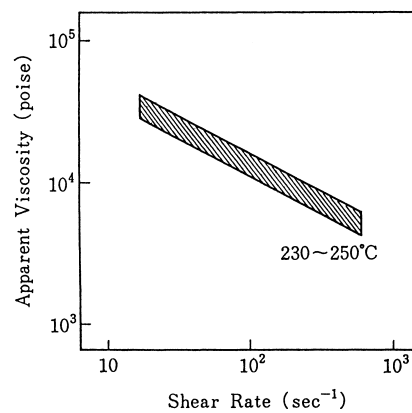
Fig. 7. Molecular weight and T_Q .

Fig. 9. Melt flow behavior of polymer.

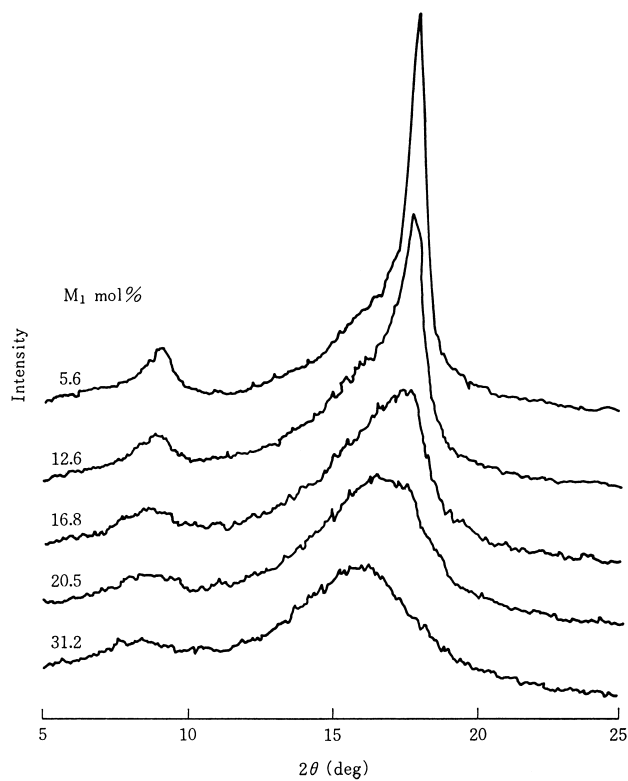


Fig. 8. X-ray spectra of copolymers.

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