Part IV

Copolymers of Vinylidene Fluoride and 1-Chloro-1,2-difluoroethylene

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The copolymers were found to range from amorphous, leathery elastomers at 20:80 CH_2CF_2:CHFCFCl ratio to crystalline plastics at 52:48 ratios and greater. To incorporate significant amounts of CF_2CH_2 into the copolymer formed in an emulsion system, it was necessary to use a fluorocarbon soap and pressures of greater than about 500 p.s.i.

THE COPOLYMER of vinylidene fluoride and 1-chloro-1,2-difluoroethylene was studied as part of a program aimed at developing elastomers with improved properties over those currently available (*1*, *2*). The analogous copolymer of vinylidene fluoride with chlorotrifluoroethylene is the commercially available Kel-F elastomer. A comparison of the two copolymers was made to help in determining the effect of replacing a CF_2 for a CHF group upon the elastomeric properties.

EXPERIMENTAL

The monomers used in this work were obtained from the production facility of Peninsular ChemResearch. They were analyzed by vapor phase chromatography over a column of the ethyl ester of Kel-F Acid 8114 (Minnesota Mining and Manufacturing Co.) on Chromosorb and found to be greater then 99% pure. Polymerizations were carried out as indicated in Table I in several types of reactors. The aerosol compatibility tubes were equipped with needle valves and either stirred magnetically or agitated in a heated 1.4-liter autoclave rocker modified to hold several such tubes. The Co^{60} irradiations were performed at a flux of about 7×10^5 röntgens per hour. The degree of crystallinity was estimated from the x-ray powder patterns. Infrared spectra of the various copolymers showed that peaks at 7.2, 11.4, and 13.1 microns increased with CH_2CF_2 content, whereas the major peak attributable to CHFCFCl was found at 9.2 microns.

RESULTS AND DISCUSSION

Copolymers with varying compositions were prepared and their properties observed. Although degree of elasticity was of particular interest, in only one instance was an even partially rubbery material obtained. Therefore, the samples were examined for crystallinity and the results compared with those for the CH_2CF_2/CF_2CFCl copolymer.

The CH_2CF_2-CF_2CFCl copolymer is amorphous at compositions containing from 40 to 85 mole % CH_2CF_2 (*3*). The corresponding copolymers with CHFCHCl, however, were crystalline even when CH_2CF_2 was present to the extent of 52 mole %. A composition containing 20 mole % CH_2CF_2 was a tough, leathery elastomer, and when the proportion of CH_2CF_2 was less all vestiges of elastomeric were lost. The copolymers with high CHFCFCl ratios, as well as the CHFCFCl homopolymer itself, were not crystalline, however. Although CHFCFCl forms an amorphous homopolymer (*5*), it is less effective than CF_2CFCl (which itself forms a crystalline homopolymer) in breaking up the inherent crystallinity of a polymer chain composed of CH_2CF_2 units. The leathery nature of the copolymers containing large proportions of CHFCFCl tend to confirm the report of the patent literature that the homopolymer has a softening temperature of 130° (*5*). Since $(CF_2CFCl)_n$ has a glass transition temperature of 45° (*4*), the replacement of CHF with CF_2 in a polymer chain has considerable effect. These results parallel those found on comparing polyvinylene fluoride, $(CHFCHF)_n$, with polyvinylidene fluoride, $(CH_2CF_2)_n$, in which the polyvinylene fluoride was less crystalline and had a higher glass transition temperature (*2*). In both cases, this is primarily a result of the

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Table I. Polymerization of Vinylidene Fluoride and 1-Chloro-1,2-difluoroethylene

Total Charge, Moles	Mole % CH_2CF_2, Charge/Copolymer	Initiation System	Pressure[a]	Reactor[b]	Time, Hours/° C.	Yield, %	$[n]_{inh}$	Remarks
0.03	50/low	A[c]	100–150	FP	96/60	50	0.09	Rather weak plastic
0.05	50/10	B[d]	100–150	FP	21/60	38	0.21	Leathery plastic
0.25	50/20	B[d]	300–500	M	120/50	56	0.8	Leathery rubber
0.21	83/85	B[d]	300–600	M	12/70	95	0.4	Crystalline plastic
0.004	50/52.5	Co^{60}	200–300	G	98/25	75	. . .	Hard pellet in bottom of reactor (95% CHF-CFCl), film in top (52% CH_2CF_2)
0.03	100	A	100–150	FP	116/60	0	. . .	
0.03	100	B	100–150	FP	24/60	10	2.06	
0.25	100	B	460	M	36/60	24	. . .	
0.003	100	Co^{60}	200–300	G	24/25	30	. . .	

[a] Initial pressure at temperature, estimated. [b] FP. Fischer-Porter aerosol compatibility tube, 75 ml.; M. Monel Hoke cylinder, 90 ml.; G. Glass Carius tube, 3 ml. [c] $K_2S_2O_8$, 0.75 part; K_2HPO_4, 2 parts; Na lauryl sulfate, 3 parts; H_2O, 200 parts; monomers, 100 parts. [d] Same as (b), except NH_4 salt Kel-F Acid 8114 replaced the Na lauryl sulfate.

loss of lateral symmetry in progressing from a polymer chain composed of CF_2 units to one composed of CHF units.

A certain amount of difficulty was encountered before even a reasonably broad spectrum of copolymers could be obtained. Since the polymerization behavior of CH_2CF_2 is little discussed outside the patent literature, it is of interest to discuss briefly the experimental findings which are summarized in Table I. In initial experiments, CH_2CF_2 showed much less tendency than CHFCFCl to enter into the copolymer. This might be due to the difficulty in emulsifying significant amounts of this low-boiling reactant (the critical temperature of which is in the vicinity of room temperature). The higher boiling chloroolefin presented no such difficulty, as it was easily liquified under the conditions used. The use of fluorocarbon soap would be expected to increase the concentration of CH_2CF_2 in the liquid phase, and the proportion found in the resulting copolymer was correspondingly higher. Carrying out the reactions under higher pressure was even more effective. A polymerization initiated by Co^{60} gamma radiation presented an interesting situation. The CHFCFCl-rich liquid phase gave a polymer containing 95% CHFCFCl, and the CH_2CF_2-rich vapor phase gave a copolymer containing 52% CH_2CF_2. A concurrent series of experiments in which the homopolymerization of CH_2CF_2 was studied further illustrated the importance of pressure and an effective emulsifier. Thus CH_2CF_2 did not polymerize using a hydrocarbon emulsifier and a relatively low pressure (100 to 150 p.s.i.). Substitution of a fluorocarbon soap resulted in a low yield of polymer being obtained. Carrying out the reaction in a metal cylinder, where a higher pressure could be tolerated, resulted in a higher yield. Thus Co^{60} was more effective, even in a reaction which took place in the gas phase.

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Generalized Correlation for Latent Heat of Vaporization

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To calculate latent heats of vaporization, a simple analytical expression without using acentric factor was developed from the Pitzer tabular correlation. Graphical solutions with a nomogram are presented. Results are compared with the existing methods.

EXTENSIVE tabular values were presented in 1955 by Pitzer and associates (*13*). Part of these values can be used for calculating quite accurately latent heats of vaporization at any temperature when acentric factor and critical temperature are known. Inasmuch as this method was not expressed in a convenient form and, to some extent, the prediction of the acentric factor by the Edmister method (*3*) is quite time consuming, it has been overlooked by many investigators for almost 10 years. This article extends their work by transforming their tabular correlation into analytical and graphical ones thereby eliminating use of the acentric factor.