Polymers from Vinyl Fluoride*

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Vinyl fluoride was prepared first by Swarts[11] in 1901, but its polymerization[8,12] was reported as difficult or impossible. Starkweather,[10] however, observed some polymerization in a toluene solution of vinyl fluoride which was saturated with monomer at −35°C. and maintained at 6000 atm. at 67°C. for 16 hr. Later, Newkirk[6] reported that vinyl fluoride was polymerized in quartz capillary tubes in the presence of ultraviolet light, benzoyl peroxide, lauroyl peroxide, or acetyl peroxide initiators under autogenous pressure. Coffman and Ford[4] prepared polyvinyl fluoride of high molecular weight and demonstrated that it can be formed into transparent films which are tough, flexible, and capable of cold drawing. This paper will describe this and the subsequent laboratory work on the synthesis of polyvinyl fluoride which led to the development of Teslar polyvinyl fluoride film (Teslar is the registered trade name for polyvinyl fluoride film, available from E. I. du Pont de Nemours and Company, Inc., Film Department, Wilmington, Delaware).

Vinyl fluoride monomer was synthesized directly from acetylene and hydrogen fluoride with the use of mercury catalysts[7,9] or indirectly from these same starting materials through the synthesis of 1,1-difluoroethane[3] and its subsequent pyrolysis to vinyl fluoride.[5] Vinyl fluoride boils at −72.2°C. at atmospheric pressure. Its critical temperature is 54.7°C. and the critical pressure is 760 psi. Monomer prepared by either method required careful purification to obtain polymers of good quality. The purification procedure included distillation to separate vinyl fluoride from 1,1,-difluoroethane, hydrogen fluoride, and other impurities. The last

traces of hydrogen fluoride were removed by passing the monomer through soda-lime towers. Acetylene was removed by scrubbing with ammoniacal cuprous chloride. A second fractionation under 40–100 psi pressure at −50° to −25°C. removed oxygen (from air contamination). Polymerization studies were conducted on monomers containing less than 5 ppm acetylene, less than 20 ppm oxygen, and negligible quantities of other impurities. The effects of impurities on polymerization will be discussed subsequently. Water employed in the polymerization experiments was deoxygenated by refluxing under nitrogen prior to use.

POLYMERIZATION STUDIES

Vinyl fluoride polymerization was investigated over the range of 35–165°C. and at pressures of 1–1000 atm. Redox systems, alkali metals, and thermally generated free radicals were investigated as initiators, but the latter gave the most attractive polymers. For most of this work, polymerizations were carried out in a 400-ml., stainless steel pressure vessel which was agitated by shaking the tube in a horizontal position or in a 1300-ml., stainless steel vessel which was rocked to provide agitation. The vessels were provided with facilities for repressuring with monomer or with deoxygenated water during reaction.

In a typical polymerization experiment, a 1300-ml. reaction vessel was charged with 0.4 g. benzoyl peroxide and was closed. The vessel was pressured with nitrogen, bled down, and evacuated through three cycles to be certain air had been removed and then was positioned in the rocking apparatus. Deoxygenated water (400 ml.) was pumped into the evacuated vessel, and 500 g. of vinyl fluoride was added. Agitation was started, and heating was begun. Vinyl fluoride was pressured to the tube during the heat-up so that the prescribed conditions of 300 atm. pressure and 85°C. temperature were reached simultaneously. The time required to reach these conditions was 1.25 hr. The vessel

was repressured as required to maintain a pressure of 300 atm. After 8 hr., no further polymerization occurred. The reaction vessel was cooled, and excess vinyl fluoride was vented. The polymer after drying weighed 260 g.

Effect of Different Initiators on Polymerization

It is known that initiator fragments represent only a small fraction of the total polymer chain, but with polyvinyl fluoride they affect profoundly polymer properties such as thermal stability and wettability. These differences in polymer properties are not merely a result of different temperature requirements for the generation of the free radicals, but apparently are associated with the solubility of the initiator in the medium and the nature of the initiator fragment that is incorporated into the polymer. Tables I and II list some of the initiators evaluated, conditions of polymerization, and brief remarks concerning the polymer produced.

Evidence of differences in the functioning of initiators was observed visually. A thick, glass-walled, liquid level gauge was modified with a stirrer and feed lines so that vinyl fluoride could be polymerized under pressure and temperature conditions similar to those employed in the metal vessels. Initiation with water-soluble initiators occurred in the water phase. The initially clear solution turned red and then changed color slowly

through red-orange to orange before becoming opaque. The polymer was obtained as a dispersion. The color change is indicative of the size of the dispersed polymer particles. On the other hand, organic soluble initiators brought about polymerization above the surface of the water. Webs of polymer appeared to grow throughout the gas phase, which as they increased in size fell and floated on the surface of the water.

Differences were noted with the initiators active at temperatures of 125°C. and above as contrasted with those active at 70–85°C. In general, polymers prepared at the higher temperature were of lower molecular weight and appeared to be more branched. Films could be pressed more easily
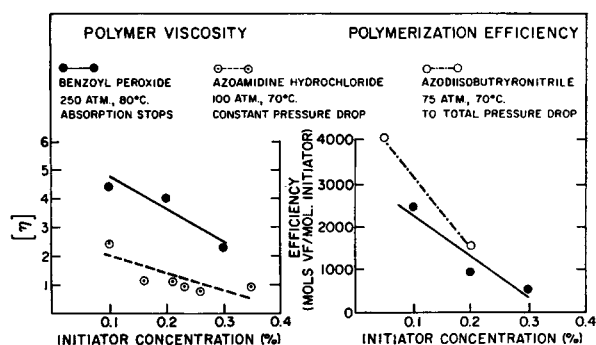

Fig. 1. Effects of initiator concentration on polymerization.

TABLE I
Initiators for Vinyl Fluoride Polymerization (35–100°C.)

Initiator	Temp., °C.	Pressure, atm.	Extent of conversion	Conversion, time, hr.	Mol. weight
α,α'-Azobis-α,γ,γ-trimethylvalero-nitrile	37	1000	High	4	High
α,α'-Azobis-α,γ-dimethylvaleronitrile	50	500	Moderate	8	Medium
α,α'-Azobisisobutyronitrile	70	70	90%	19	High
α,α'-Azobisisobutyramidine hydrochloride	70	100	40%	4	High
Benzoyl peroxide	80	250	37%	13	Very high
Ammonium persulfate	85	250	33%	2	Medium

TABLE II
Initiators for Vinyl Fluoride Polymerization (above 100°C.)

Initiator	Temp., °C.	Pressure, atm.	Extent of conversion	Conversion time, hr.	Mol. weight
α,α'-Azodicyclohexane carbonitrile	115	175	32%	1.5	Moderately high
Diethyl peroxide	122	600	Good	14.5	Medium
tert-Butyl peroxide	140	500	Good	0.5	Medium
2(2'-Hydroxyethylazo)-2-ethylbutyronitrile	145	250	Good		Medium

from these high temperature polymers than from benzoyl peroxide polymers.

Initiator concentration influenced molecular weight as indicated by intrinsic viscosity values. With benzoyl peroxide in aqueous medium, an increase in the concentration of peroxide at 80–90°C. and 250 atm. pressure resulted in decreased initiator efficiency and intrinsic viscosity of the polymer (Fig. 1). Similar results were observed with azo initiators.

Effect of Temperature

It is known that a change in temperature affects the decomposition rate of initiators to free radicals, and this, in turn, affects polymerization rate.[1,2] The data for vinyl fluoride shown in Figure 2 demonstrate that initiator efficiency reaches a maximum and then falls off. With α,α'-azobis-isobutyronitrile, this temperature of maximum initiator efficiency appears to be independent of pressure within the range studied.
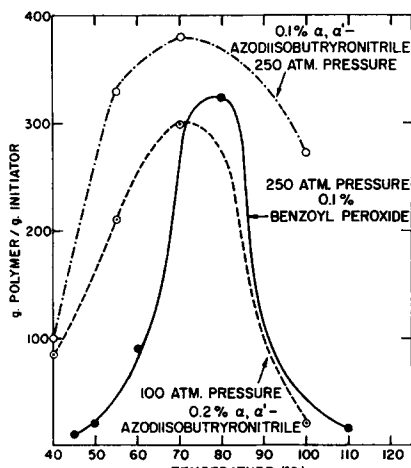
Fig. 2. Polymer yield as a function of temperature.

Polyvinyl fluoride prepared with a given initiator had generally lower melt viscosity as the polymerization temperature was increased. This effect probably results from a combination of more rapid chain termination (lower molecular weight) and increased chain branching at the higher temperature.

Effect of Pressure

In addition to increasing the rate of polymerization, higher pressure favored higher inherent viscosity of the polymer, and more efficient use of initiator. Figures 3 and 4 illustrate data obtained
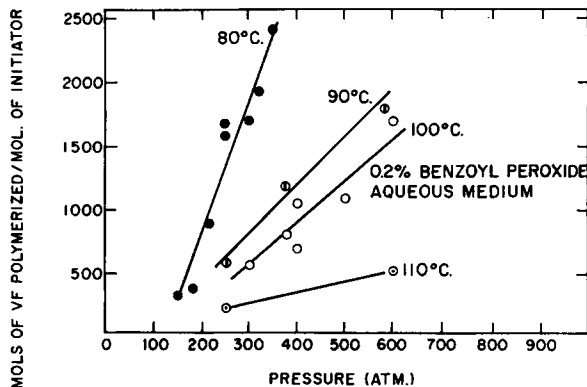
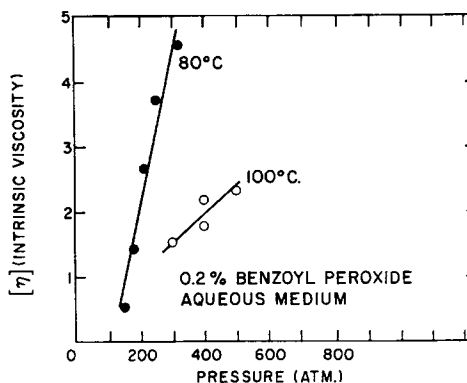Fig. 3. Effect of polymerization pressure on initiator frequency.

Fig. 4. Effect of polymerization pressure on viscosity.

with benzoyl peroxide initiator, but other initiators showed similar trends.

Effect of Impurities

Air (oxygen), acetylene, and 1,1-difluoroethane are likely impurities in vinyl fluoride monomer. In order to determine the effects of these, mixtures of vinyl fluoride with different quantities of impurities were polymerized. With the use of 0.2% benzoyl peroxide initiator at 900 atm. and 80–100°C., 500 ppm oxygen in the monomer inhibited slightly the polymerization reaction, but 135 ppm oxygen appeared to promote the polymerization (Fig. 5). The presence of 2% acetylene in the vinyl fluoride strongly inhibited polymerization, the low molecular weight polymer which was brittle and readily soluble in hot cyclohexanone being obtained in only 3% yield. At a concentration of 1000 ppm, acetylene accelerated polymerization, over 99% conversion of monomer to polymer being obtained. The reaction velocity was almost uncontrollable, and the polymer was crosslinked and insoluble.
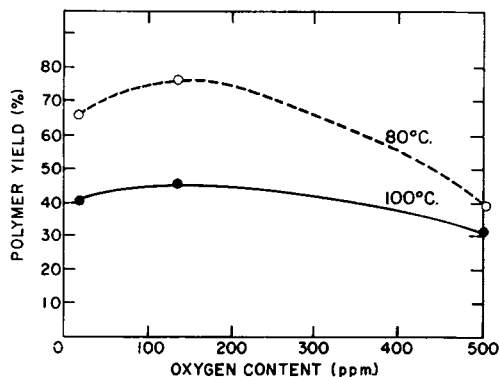
Fig. 5. Effect of oxygen on polymer yield.

Polymerization of oxygen- and acetylene-free vinyl fluoride monomer containing 2.5% 1,1-difluoroethane gave a normal yield of polymer with 0.2% benzoyl peroxide initiator in a methanol/water (40/60) medium at 250 atm. and 80°C. Film properties and molding characteristics indicated that the system had not been affected by this impurity.

Effect of Telogens

A number of chain-terminating substances (telogens) were evaluated as molecular weight control agents (Fig. 6). The use of controlled amounts of telogens was one of the best ways to reduce melt viscosity without undue sacrifice in toughness.
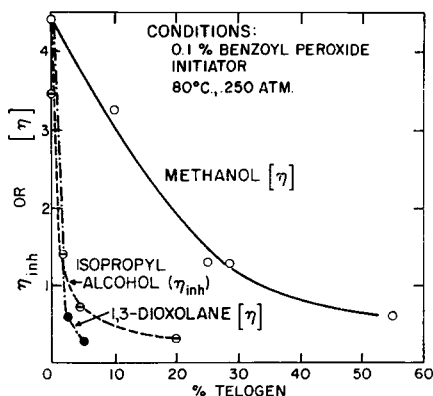

Fig. 6. Effect of telogens on vinyl fluoride polymerization.

Use of Media Other Than Water

A number of organic solvents were examined as polymerization media to determine their effect on vinyl fluoride polymerization. Media other than water showed a tendency to telomerize with the vinyl fluoride causing drastically reduced molecular weight.

The tert-butyl peroxide-initiated polymerization of vinyl fluoride in benzene medium at 140°C. and 800 atm. pressure yielded polymer with an inherent viscosity of 1.77. However, the conversion was low, and the polymer was deficient in thermal stability. Diethyl peroxide also gave low conversions of polymer in benzene solution at 120–130°C. and 300–900 atm. using 0.1% initiator. The highest conversion of monomer to polymer (17%) was noted at the highest pressure investigated (900 atm.). Films prepared from these polymers were all shock brittle.

POLYMER PROPERTIES

Polyvinyl fluoride is a high-melting, chemically inert polymer which can be fabricated into tough, weather-resistant films, fibers, and moldings. The density of the polymer is 1.39 g./cm.[3] Many of the properties may be modified by varying polymerization procedure.

Solubility

High molecular weight polyvinyl fluoride is not soluble in solvents at temperatures below 100–110°C. Above 100°C., N-substituted amides, dinitriles, ketones, tetramethylene sulfone, and tetramethylurea were found to be solvents, and films were cast from solutions in these solvents. Dimethylformamide and tetramethylurea were outstanding solvents and were employed in laboratory film-casting experiments. High viscosity polymer, such as that obtained from benzoyl peroxide polymerization systems, having intrinsic viscosity in the range of 3–4 was soluble in dimethylformamide to the extent of 10–15% at 110°C. and above. Polymers of lower molecular weight (e.g., those prepared in media other than water or.in aqueous systems containing telogens) were more soluble. At room temperature or slightly above, polyvinyl fluoride prepared with benzoyl peroxide or with azonitrile initiator formed gels when stirred vigorously in dimethylformamide. Similar gel structures were obtained when polymer solutions were cooled below 100°C. Polymers prepared with water-soluble initiators showed less tendency to form gels and could be slurried with solvents without forming gels.

The insolubility of polyvinyl fluoride in solvents at ordinary temperatures has made plasticization of the polymer difficult. A number of materials were compatible with the polymer at 100–110°C. in ratios as high as 1:1, but on cooling to room temper-

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TABLE III

Molecular Weight of Polyvinyl Fluoride (by Osmotic Pressure)

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Polymerization conditions	Dimethylformamide $\bar{M}_n$	γ-Butyrolactone		Dimethylacetamide	
		$\bar{M}_n$	η_{inh}	$\bar{M}_n$	η_{inh}
Bz_2O_2, 40% MeOH 80°C. 250 atm.	45,600	45,500	0.79		
Azoamidine hydrochloride 0.25% isopropyl alcohol, 75°C., 100 atm.	67,800	64,200	1.13	67,000	1.23
tert-Butyl peroxide, 140°C., 250 atm.		84,600	0.98		

ature they were exuded. Dibutyl phthalate and tricresyl phosphate were among plasticizers that were retained by the polymer to the extent of 5–10%. This amount of plasticizer lowered the softening temperature of the polymer without imparting rubbery characteristics.

Molecular Weight

Variations in polymerization conditions are reflected in solution viscosity and in molecular weight values. Accordingly, the molecular weights of polyvinyl fluoride prepared under different conditions were determined and correlated with viscosity measurements. Solubility characteristics restricted somewhat the selection of polymers whose molecular weights could be determined by osmotic pressure and therefore tagged initiators were used to obtain independent molecular weight values. Molecular weight determinations were also made by ultracentrifuge techniques.

Osmotic pressure molecular weights were determined in solution at 100°C. with the use of a cellophane membrane conditioned through acetone to the polyvinyl fluoride solvent. Table III lists the values found for telogen-modified benzoyl peroxide and α,α'-azobisisobutyramidine hydrochloride polymers as well as for the high-temperature, unmodified tert-butyl peroxide-initiated polymer. Because of the difficult solubility problems with the polymer, several determinations were made on the same polymer with different solvents. The data indicate that molecular weight by this technique was independent of the solvent used. Anomalies between molecular weight and viscosity values may be caused by solubility or perhaps polymer branching. The molecular weight of the azoamidine hydrochloride polymer was determined by ultracentrifuge methods to be 119,000. The difference between this molecular weight (M_w),

and molecular weight values determined by osmotic pressure (M_n) is normal.

The use of radioactive carbon gave independent values for molecular weight. Experimentally, vinyl fluoride was polymerized in the presence of tagged initiator or tagged telogen. Polymers were isolated in the usual manner. Samples of the polymers were burned in oxygen, and the activity of the carbon dioxide formed was determined. Molecular weights were calculated, each chain being assumed to contain one initiator fragment. When tagged isopropyl alcohol telogen was added, molecular weight calculations were based on one molecule

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TABLE IV

Molecular Weight of Polyvinyl Fluoride (Using Tagged Initiator)

0.2% Benzoyl Peroxide Initiator, 250 atm. Vinyl Fluoride

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Polymerization temperature, °C.	Intrinsic viscosity	Molecular weight
85	4.40	180,000
95	3.50	169,000
110	1.47	58,000

of alcohol for each polymer chain. This assumption appeared to be valid: polymers prepared under identical conditions, but differing in that in one the initiator was tagged, whereas in the other isopropyl alcohol was tagged, gave similar values for molecular weight. Experiments 1, 2, and 3 (Table IV) demonstrate that molecular weight decreases with increasing temperature of polymerization in the presence of benzoyl peroxide initiator. Experiments 4 through 8 illustrate the decrease in molecular weight as telogen is increased (Table V).

Melting points of the polymer were determined with a differential thermal analyzer. Thermal effects were balanced against an alumina control, and the differential temperature between the sample

TABLE V
Molecular Weight of Polyvinyl Fluoride (Using Tagged Initiator)
0.1% α,α'-Azobisisobutyramidine Hydrochloride, 75°C., 100 atm., Water Medium

Modifier	Intrinsic viscosity	Molecular weight
None	1.28	90,800
0.5% Isopropyl alcohol	1.91	55,300
0.5% Isopropyl alcohol[a]	1.78	57,530
1.0% Isopropyl alcohol[a]	0.94	27,600
1.0% Isopropyl alcohol	1.20	20,100

[a] Isopropyl alcohol tagged; initiator not tagged.

and the control was amplified and compared by means of a recording potentiometer. Unmodified benzoyl peroxide polymers having a wide range of viscosity melted near 198°.

Piston rheometer studies were carried out on various samples of modified and unmodified polymer. Unmodified samples prepared with initiators active in the range of 50–100°C. had viscosities too high to measure. However, the melt viscosity of polymers prepared at 130°C. and above or of telogen-modified polymer was easily determined. A polymer prepared with benzoyl peroxide in 40% methanol had an apparent melt viscosity of 6×10^4 poises at 210°C. under a stress of 9.48×10^5 dynes/cm.^{2}.

Fabrication Techniques

Compression molding into films and bars of high viscosity polymers was best carried out at temperatures above 200°C. in order to obtain maximum impact strength. Properly fused bars prepared from high viscosity polymer had impact strengths in excess of 10 ft.-lb./in. of notch with tensile strengths in the range of 4000–8000 lb./in.^{2}. Conditions of temperature and pressure had to be controlled closely to prevent polymer decomposition. Small amounts of acid acceptors stabilized the polymer during fabrication.

Injection molding was also investigated. Polymers of high molecular weight could not be molded in the absence of large quantities of stabilizers and plasticizers, and some of the polymers decomposed violently during molding. However, stabilized medium viscosity polymers such as were prepared with α,α'-azobisisobutyronitrile initiator in methanol/water (40/60) were injection-molded into bars having impact strengths (Izod) in excess of 3 ft.-lb./in. of notch and with softening points near

155°C. The translucent moldings were completely undistorted after three weeks in boiling water.

Solution film casting of polyvinyl fluoride was also successfully developed. The polymer was dissolved in solvents such as dimethylformamide at 125–130°C. An 8% solution was found to be satisfactory; higher concentrations were usually too viscous to handle. Films were prepared by casting with a doctor knife on a chromium-plated casting plate heated to 120–130°C. Drying was carried out slowly to avoid wrinkles in the film. After removal from the plate the films were transparent but somewhat hazy. Heating momentarily above 250°C. and quenching the films improved clarity.

FILM PROPERTIES

High molecular weight polyvinyl fluoride film has high tensile strength, good toughness, and excellent clarity. Further, its resistance to weathering is outstanding for a clear film. Samples exposed at an angle of 45° to the horizontal facing south at Hialeah, Florida, and Wilmington, Delaware, maintained much of their original toughness over a ten-year test (Table VI). At the end of this time, the samples were still cold-drawable, indicating that embrittlement had been extremely slow.

TABLE VI
Durability of Polyvinyl Fluoride

| | High viscosity polymer | |
Exposure time, yr.	Tensile strength, lb./in.^{2}	Elongation, %
Florida exposure, 45° to horizontal, facing south.		
0	8500	421
1/2	7600	418
1	4400	212
2	8900	438
5	6900	417
10	4800	232
Wilmington exposure		
0	7200	388
10	8300	351

CONCLUSIONS

Vinyl fluoride has been polymerized by free radicals into attractive polymers. Polymer properties have been described generally and in terms of the effects of different variables. Polymers have been fabricated into tough, molded products by melt techniques and into films by solution casting. Polyvinyl fluoride films are clear, tough, and re-

sistant to chemicals and solvents. In addition, they possess outstanding weatherability.

Professor J. J. Martin of the University of Michigan determined the physical constants for the vinyl fluoride monomer. A. L. Barney, J. R. Downing, W. D. Nicoll, J. H. Peterson, H. S. Rothrock, and C. G. Wortz of the Central Research Department of E. I. du Pont de Nemours and Company also contributed to the information included in this paper.

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Synopsis

The free-radical polymerization of vinyl fluoride has been studied with the use of organic peroxide and azo initiators over the temperature range of 60–150°C. and at pressures of 75–1000 atm. Molecular weights of the polymers by osmotic pressure or radiotracer techniques were found to vary over the range of 45,000 to 180,000 depending on polymerization conditions employed. Stabilized high molecular weight polyvinyl fluoride may be compression-molded into tough, high-impact strength bars, or the unstabilized material may be cast into films from solvents such as dimethylformamide.

The films, which may be cold drawn, are tough, brilliantly clear, and have tensile strengths near 8000 lb./in.² They are also extremely resistant to weathering, maintaining clarity and cold drawability even after ten years' exposure in Florida.

Résumé

On a étudié la polymérisation radicalaire du fluorure de vinyle en se servant comme initiateurs de peroxydes organiques et de dérivés azoïques dans le domaine de température allant de 60° à 150°C. et à des pressions variant de 75 à 1000 atm. Les poids moléculires des polymères déterminés par pression osmotique et par la technique des traceurs radioactifs varient de 45,000 à 180,000 suivant les conditions de polymérisation. Le fluorure de polyvinyle stabilisé et de haut poids moléculaire peut être moulé par compression en barres dures et de grande force d'impact; la substance non stabilisée peut également être mise en films à partir de solvants tels que le diméthylformamide. Les films qui peuvent être étirés à froid sont durs, lisses et brillants et possèdent une résistance à la tension d'à peu près 8000 livres/pouce carré. Ils sont aussi extrêmement résistants aux agents atmosphériques, gardent leur transparence et leur possibilité d'étirement à froid même après dix ans d'exposition en Floride.

Zusammenfassung

Die radikalische Polymerisation von Vinylfluorid wurde mit organischen Peroxyden und Azostartern im Temperaturbereich von 60–150°C und bei Drucken von 75 Atm bis 1000 Atm untersucht. Die Molekulargewichte der Polymeren wurden osmotisch und durch radioaktive Markierung bestimmt und lagen in Abhängigkeit von den verwendeten Polymerisationsbedingungen im Bereich von 45 000 bis 180 000. Stabilisiertes, hochmolekulares Polyvinylfluorid kann zu zähen Stäben mit hoher Schlagfestigkeit verpresst werden oder das unstabilisierte Material kann aus Lösungsmitteln wie Dimethylformamid zu Filmen gegossen werden. Die Filme, die kalt gereckt werden können, sind zäh, von einer brillanten Klarheit und besitzen eine Zugfestigkeit um 8000 lb./sq. in. Sie sind auch gegen Bewitterung äusserst widerstandsfähig, wobei sie ihre Klarheit und Reckbarkeit in der Kälte auch nach einer Bewitterungsdauer von zehn Jahren in Florida beibehalten.