

similar order of the reactivity has already been noted in the series of 2-oxazolines,⁹ e.g., $\sim\text{OZO}^+ > \sim\text{PhOZO}^+ > \sim\text{MeOZO}^+$. In addition, the entropy factor (or the frequency factor, A_p) seems to be important as well. It has been established that k_p values were not much affected by changing of the solvent from nitrobenzene to CD_3CN . Therefore, it is meaningful to compare k_p values at 100° in nitrobenzene and CD_3CN in Table II. These values of five monomers are in the range of 0.00025–1.3 l./mol sec).

Finally, the effect of a methyl group on k_i and k_p values is another point of interest. Introduction of a methyl group at the 2 position of the OZI ring made the k_i value more than double but made the k_p value decrease by 5.7 times (Table II). From the above discussion, this behavior may be ascribed to the decreased ring-opening tendency of 2-

methyl-5,6-dihydro-4H-1,3-oxazinium ion (4 and 6) in comparison to that of unsubstituted 5,6-dihydro-4H-1,3-oxazinium ion.

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Poly(2-vinylfluorenone). I. Synthesis and Polymerization of 2-Vinylfluorenone

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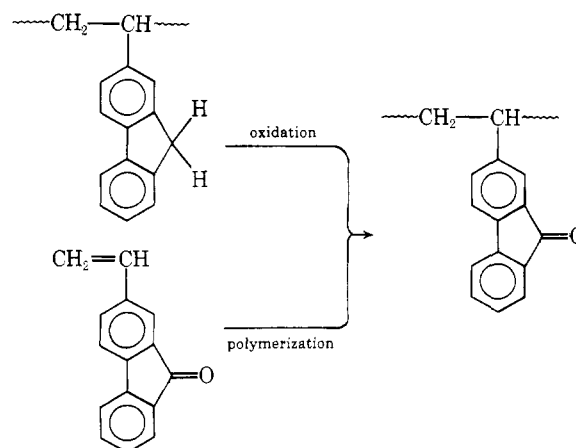
ABSTRACT: The synthesis and polymerization characteristics of the new monomer, 2-vinylfluorenone, are reported. Previous attempts to prepare 2-vinylfluorenone polymers by oxidation of poly(2-vinylfluorene) were unsuccessful, leading to low yields of soluble copolymer products containing approximately 50 mol % of fluorenone units. Using an improved oxidation procedure we have succeeded in increasing the degree of oxidation of fluorene to fluorenone groups to 90% without any loss of solubility. The monomer synthesis and polymerization, however, provide the only unequivocal route to homopolymers of 2-vinylfluorenone. 2-Vinylfluorenone can be readily polymerized and copolymerized by free-radical techniques to give high molecular weight, $\bar{M}_n > 10^5$, soluble polymers. The monomer does not polymerize by cationic or anionic methods. Free-radical polymerization of 2-vinylfluorenone in solution exhibits a very unusual concentration effect which remains unexplained.

Vinyl polymers containing aliphatic and aromatic carbonyl groups have been widely studied in recent years because of their relevance to photodegradation and photostabilization phenomena. Guillet and his coworkers have reported the photochemical behavior of a variety of poly(ethylene-co-carbon monoxide) materials¹ and poly(alkyl and aryl vinyl ketones).^{2,3} Geuskens, *et al.*, have also studied energy-transfer processes and photolytic reactions in carbonyl containing polymers such as poly(methyl vinyl ketone),⁴ poly(phenyl vinyl ketone),⁵ and poly(vinylbenzophenone).⁶

Braun first proposed⁷ a synthetic procedure for preparing a fluorenone-containing vinyl polymer: amyl nitrite oxidation of poly(2-vinylfluorene) to the corresponding poly(2-vinylfluorenone). Gipstein, Hewett, and Need⁸ investigated this synthetic route and developed a more direct oxidation procedure using chromium trioxide in glacial acetic acid. Oxidation of poly(2-vinylfluorene) using these conditions gave a product from which a soluble fraction could be extracted. Analysis of the polymer showed it to be an approximately 50:50 copolymer of 2-vinylfluorene and 2-vinylfluorenone. The insoluble fraction gave a chemical analysis more consistent with a higher degree of oxidation, *i.e.*, a poly(2-vinylfluorenone) homopolymer. Similarly, oxidation of copolymers containing 2-vinylfluorene gave soluble and insoluble product mixtures, the soluble fractions consisting of terpolymers resulting from partial oxidation.

The very appreciable changes in the polymer molecular weights and molecular weight distributions, and the high yields of insoluble products, clearly indicate the severity of these oxidation procedures. Using much milder oxidation

conditions, *e.g.*, benzyltrimethylammonium hydroxide: oxygen in pyridine at 0°, we have been able to oxidize poly(2-vinylfluorene) to a much higher degree (80–90%) in high yield and without any appreciable molecular weight variations and insolubilization. However, even under optimum conditions it was not possible to achieve complete oxidation, *i.e.*, a homopolymer of 2-vinylfluorenone. This was achieved, however, *via* synthesis and polymerization of the new monomer, 2-vinylfluorenone.

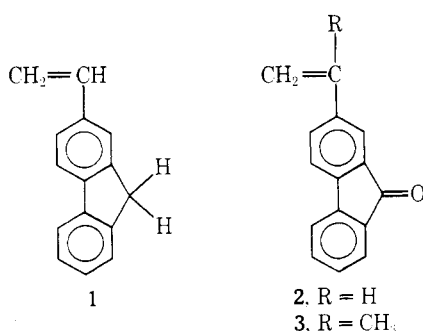


Experimental Section

2-Vinylfluorene (1) was synthesized from fluorene-2-carboxaldehyde (Aldrich) using the Wittig procedure. Triphenylmethylphosphonium bromide (36 g; 0.1 mol) in 500 ml of dry THF was

treated under nitrogen with 90 ml of a 1.1 M solution of *n*-butyllithium in hexane and stirred for 2 hr. A solution of 19.4 g (0.1 mol) of fluorene-2-carboxaldehyde in 100 ml of THF was added dropwise and the final mixture was refluxed for 1.5 hr. One liter of hexane was added to the cold solution and the precipitate filtered off. The filtrate was evaporated and the residue chromatographed on alumina (Woelm neutral) using hexane to give 15 g (75%) of product. Recrystallization from hexane gave 2-vinylfluorene as colorless plates, mp 139–140° (lit.⁹ 133–134°): nmr (CCl₄) δ 3.77 (s, 2, CH₂); 5.07–5.23, 5.25–5.81, 6.46–6.62, 6.74–6.93 (d, 3, CH=CH₂); 7.4 (m, 7, aromatic). *Anal.* Calcd for C₁₅H₁₂: C, 93.71; H, 6.29. Found: C, 93.60; H, 6.23.

2-Vinylfluorene (2). 2-Vinylfluorene (10 g; 0.05 mol) was dissolved in 800 ml of pyridine and cooled to 0°. Benzyltrimethylammonium hydroxide (0.5 ml of a 40% solution) (TRITON B)¹⁰ in pyridine was slowly added while air was bubbled through the reacting solution. The initially formed red coloration faded over a period of 1–2 hr and the solution was poured into water and extracted with benzene to yield 9 g (90%) of a yellow solid. This residue was chromatographed on alumina (Woelm basic) and eluted with benzene. Recrystallization from hexane gave 2-vinylfluorene as a pale yellow material, mp 69–70°: nmr (CCl₄) δ 5.16–5.33, 5.55–5.88, 6.43–6.59, 6.72–6.90 (d, 3, CH=CH₂); 7.3 (m, 7, aromatic); ir (Nujol) 910–990 (vinyl) and 1700 cm⁻¹ (C=O). *Anal.* Calcd for C₁₅H₁₀O: C, 87.35; H, 4.89; O, 7.75. Found: C, 87.36; H, 5.00; O, 7.64



α -Methyl-2-vinylfluorene (3). Conversion of 2-acetylfluorene (Aldrich Chemical) to the vinyl derivative was achieved in 70% yield using the Wittig procedure described in the synthesis of 2-vinylfluorene. Recrystallization of the product from hexane gave α -methyl-2-vinylfluorene as tan colored crystals, mp 155–156°. This monomer was oxidized to the corresponding fluorenone derivative by the procedure described for the synthesis of 2-vinylfluorene. Recrystallization of the product from hexane gave α -methyl-2-vinylfluorenone as pale yellow crystals, mp 76–77°: nmr (CCl₄) δ 2.20 (s, 3, CH₃), 5.16–5.52 (d, 2, =CH₂), 7.5 (m, 7, aromatic). *Anal.* Calcd for C₁₆H₁₂O: C, 87.24; H, 5.49, O, 7.27. Found: C, 87.14; H, 5.50; O, 7.36.

Polymerization Reactions. All polymerization reactions were carried out using standard procedures. Reagents were carefully purified and dried and actual polymerization runs were carried out under nitrogen or under vacuum. Polymers were isolated by precipitation from methanol and purified by at least two dissolution/precipitation steps followed by pumping under vacuum.

Polymer Characterization. The polymer molecular weights were determined at 25° by conventional viscometric techniques and osmometry. A Hewlett-Packard 502 high speed membrane osmometer with gel cellophane membranes (type 450D and 600D from Arro Labs) and DMF as solvent was used to determine \bar{M}_n values. A Waters Model 200 gel permeation chromatograph was employed to measure the molecular weight distribution. The instrument was calibrated for THF as solvent with standard polystyrene samples (Pressure Chemical). Intrinsic viscosities, $[\eta]$, and \bar{M}_n values were calculated in the standard manner.

Oxidation Procedures. The poly(2-vinylfluorene) used in the oxidation reactions was prepared in methylene chloride at –30° using BF₃·Et₂O as initiator. A typical polymer had the following molecular weight, $\bar{M}_n \sim 350,000$ and MWD ~ 5 . In a typical oxidation reaction 5 g of poly(2-vinylfluorene) ($\bar{M}_n \sim 350,000$, MWD ~ 5) was dissolved in 800 ml of dry pyridine and cooled to 0°. A stream of dry air was bubbled through the solution and a 40% solution of benzyltrimethylammonium hydroxide (TRITON B) in pyridine was slowly added until no further red coloration was produced (0.3–0.4 ml). The polymer was precipitated from methanol. The polymer, 4.8 g and 95% yield, was pale yellow in color.

Elemental and uv spectroscopic analysis showed it to be approximately a 70:30 copolymer of 2-vinylfluorene–2-vinylfluorene. The degree of oxidation could be increased by further treatment of this copolymer with TRITON B using dimethylformamide as solvent. The maximum conversion which was attained by this method resulted in an approximate 90:10 2-vinylfluorene–2-vinylfluorene copolymer. Virtually no insoluble polymer was produced in this oxidation procedure but a change in the molecular weight was noted (\bar{M}_n 200,000, MWD ~ 10) indicating some chain scission and chain coupling even under these fairly mild conditions.

Results and Discussion

Oxidation of Poly(2-vinylfluorene). The oxidation of poly(2-vinylfluorene) using the amyl nitrite method of Braun⁷ and the chromium trioxide–acetic acid procedure of Gipstein, et al.,⁸ gave low yields of copolymers. Attempts to increase the degree of oxidation resulted in excessive cross-linking and insoluble products.

A number of alternative oxidative techniques were investigated in this present study and the best results were obtained using the TRITON B reagent. Polymer concentration and temperature were optimized (see the Experimental Section) in terms of degree of oxidation and solubility of product. A two-stage oxidation procedure gave the best results. The copolymer formed in the first reaction was more soluble in *N,N*-dimethylformamide (DMF) and further oxidation could be effected. The solvent effect probably reflects the polymer conformation in solution and the accessibility of the reacting sites. All attempts to increase the degree of oxidation beyond the 90% maximum resulted in a drastic loss of soluble polymer and it was obvious that a homopolymer of poly(2-vinylfluorene) could not be achieved by this procedure.

Synthesis and Polymerization of 2-Vinylfluorene. In view of the limitations of the oxidation route, the monomer synthesis and polymerization approach clearly provides the only unequivocal route to a homopolymer of vinylfluorenone.

Free-Radical Polymerization. Initial attempts to polymerize 2-vinylfluorenone solution using free-radical initiation over the temperature range –70 to 90° gave low conversion, low molecular weight products. Monomer recovery was high and monomer purity did not appear to be the cause of this anomalous finding. The related monomer, α -methyl-2-vinylfluorenone, gave no polymer using free radical initiators at temperatures above 0°. At lower temperatures solubility problems were encountered but generally low yields of low molecular weight polymers were obtained with high recovery of unreacted monomer.

α -Methyl-2-vinylfluorenone is a 1,1'-disubstituted monomer possessing two sterically bulky groups and the absence of polymer formation above 0° could result from a ceiling temperature effect. Since α -methyl styrene is difficult to polymerize at temperatures above 0°, it is not unexpected that this fluorenone monomer does not polymerize in this temperature range. The inability to effect the polymerization of 2-vinylfluorenone was, however, unexpected.

Vinyl aliphatic ketones (methyl vinyl and methyl isopropenyl ketone) undergo facile radical polymerization in solution to high molecular weight products.¹¹ There are only a few reports on the polymerization of vinyl aromatic ketones. Marvel¹² and Mulvaney¹³ studied the free-radical polymerization of acrylophenone in bulk and in solution and reported formation of high molecular weight polymers. Although no detailed kinetic analyses were performed, there was no indication of any anomalous, e.g., chain transfer, effects arising from the aromatic carbonyl function. Geuskens¹⁴ mentioned the synthesis and polymerization of 4-vinylbenzophenone but no experimental details were pro-

Table I
Free-Radical Polymerization of 2-Vinylfluorenone

Procedure	Initia- tor ^b	Temp, °C	Time, hr	Con- ver- sion, %	Poly- mer DP
Solution ^a	AIBN	60 to 90	24	<10	<50
	BMPP	30	24	<10	<50
	BP/EtAlCl ₂	0 to -70	48	<10	<50
Bulk	AIBN	75 to 100	3	90	>500
	BP	75 to 100	3	90	>500
Emulsion	K ₂ S ₂ O ₈	80 to 90	5	90	>500

^a Solvents used were toluene, benzene, and tetrahydrofuran with [S]/[M] ratios in the range of 1 to 50. DP of 500 corresponds to $\bar{M}_n \sim 100,000$. ^b BMPP = bis(2-methylpentanoyl) peroxide, BP = benzyl peroxide.

vided. Braun, *et al.*,¹⁵ found that soluble poly(4-vinylbenzophenone) was only formed at very low conversions; the cross-linking efficiency appeared to be extremely high but no explanations were given. This monomer is structurally closely related to vinylfluorenone but the resonance/inductive effects are somewhat different.

Recent work of Pinazzi and Fernandez^{16,17} on the synthesis and free-radical polymerization behavior of a number of ring-substituted 4-vinylbenzophenones somewhat parallels our observations for 2-vinylfluorenone. In their case, bulk polymerization gave insoluble polymer while polymerization in the presence of too high a concentration of solvent (*i.e.*, [S]/[M] ratios > 15–20) only proceeded to a very low conversion, less than 10%. With 2-vinylfluorenone monomer the solvent effect appears to be even more dramatic. Polymerization of 2-vinylfluorenone in the bulk at temperatures above 75° achieved 60–80% conversion in 2–3 hr. High molecular weight polymers, $\bar{M}_n > 10^5$, which are readily soluble in organic solvents, *e.g.*, THF and chloroform, are produced with no evidence for any cross-linked gel material. The presence of even small amounts of diluent, 5–10 mol %, brings about appreciable decreases in the conversion of molecular weight of the polymer. Emulsion polymerization of the pure monomer (using a typical recipe) at temperatures around 80° gave high yields (80–90%) of soluble, high molecular weight polymer ($\bar{M}_n > 10^5$), and this was found to be the most convenient polymerization procedure. Here again the presence of solvent, *i.e.*, polymerization within an emulsified droplet containing a solvent such as benzene, caused a dramatic reduction in the conversion and polymer molecular weight. α -Methyl-2-vinylfluorenone polymerized under similar conditions failed to produce any polymer.

The free-radical polymerization characteristics of 2-vinylfluorenone are summarized in Table I. The facile polymerization of 2-vinylfluorenone in the bulk contrasts strongly with its polymerization in the presence of diluents. The effect is not correlated with the chain transfer characteristics of the solvent but must reflect some stability/reactivity/selectivity of the 2-vinylfluorenone radical. The very similar phenomenon reported for vinylbenzophenone monomers makes it tempting to attribute the effect to the aromatic carbonyl function. However, there is no evidence for any complexing or association phenomena which would manifest itself in this manner and we can offer no rationale for these experimental observations.

Ionic Polymerization. The ionic polymerization of alkyl vinyl ketones has been investigated in detail and was reviewed by Lyons.¹¹ Mulvaney reported the anionic polymerization of acrylophenone¹³ and α -methacrylophenone.¹⁸ The anionic polymerization of vinyl ketones is character-

Table II
Molecular Weight Characterization of
Poly(2-vinylfluorenone)

Sam- ple	Solvent ^a	Osmom- etry		Gpc ^b		
		$[\eta]$, dl/g	$\bar{M}_n \times 10^4$	$A_n \times 10^3$	$A_w \times 10^3$	MWD
1	DMF	0.36	22			
	THF	0.36		3.9	11.40	2.8
	Chloroform	0.74				
2	TCE	1.14				
	DMF	0.25	12			
	THF	0.27		2.0	5.2	2.5
	Cyclohexanone	0.29				
3	Chloroform	0.45				
	TCE	0.68				
	DMF	0.11	3.5			
	THF	0.11		0.54	0.75	1.5
	TCE	0.27				

^a DMF = *N,N'*-dimethylformamide, THF = tetrahydrofuran, TCE = 1,1,2,2-tetrachloroethane. ^b $\bar{M}_w = A_w \times 60$, $\bar{M}_n = A_n \times 60$, MWD = \bar{M}_w/\bar{M}_n .

ized by a direct stabilization of the carbanion through a conjugative effect of the carbonyl function and is more typical of an enolate ion system.

Boron trifluoride and the corresponding etherate in methylene chloride or chlorobenzene in the temperature range -70 to -30° did not initiate the polymerization of 2-vinylfluorenone or the α -methyl derivative and monomer recovery was high. Similarly trace amounts of protonic acids were ineffective and it was concluded that these monomers do not readily undergo cationic polymerization. Treatment of 2-vinylfluorenone in a polar (THF) and non-polar (benzene, hexane) solvent, in the temperature range -70 to 25°, with *n*-butyllithium also did not result in polymer formation. The yellow colors produced in THF may have resulted from anomalous electron-transfer reactions or carbonyl addition reactions between the fluorenone monomer and initiator. Only monomer was recovered from these systems indicating the absence of anionic polymerization. The vinyl group in the 2 position is not directly conjugated with the carbonyl of the fluorenone moiety and stabilization of the carbanion is not anticipated.

Copolymerization of 2-Vinylfluorenone. The copolymerization characteristics of 2-vinylfluorenone were briefly investigated. Free-radical copolymerization with styrene and *N*-vinylcarbazole was studied in the absence of solvent using AIBN at 80°. Copolymer compositions were determined from elemental analysis and ir and uv spectroscopy, and the reactivity ratios were found to reflect the strong tendency for the 2-vinylfluorenone radical to add to its own monomer, *i.e.*, $r_1 > 1$ ($M_1 = 2$ -vinylfluorenone) and $r_2 < 1$.

Solution Characteristics. Poly(2-vinylfluorenone) produced by high conversion bulk or emulsion polymerization is readily soluble in a number of common organic solvents. This is to be contrasted with the polymerization of 4-vinylbenzophenones where insoluble products are common, presumably resulting from facile cross-linking through the aromatic ketone function. In order to verify the apparent linear nature of the poly(2-vinylfluorenone), based on their solubility behavior, the solution properties of a series of polymers of different molecular weight were investigated and are reported in Table II.

The Mark-Houwink parameters for poly(2-vinylfluorenone) are very similar to those reported for a number of vinyl aromatic polymers possessing bulky pendant groups;¹⁹ *K* values fall in the range 1 to 4×10^{-4} and *a*

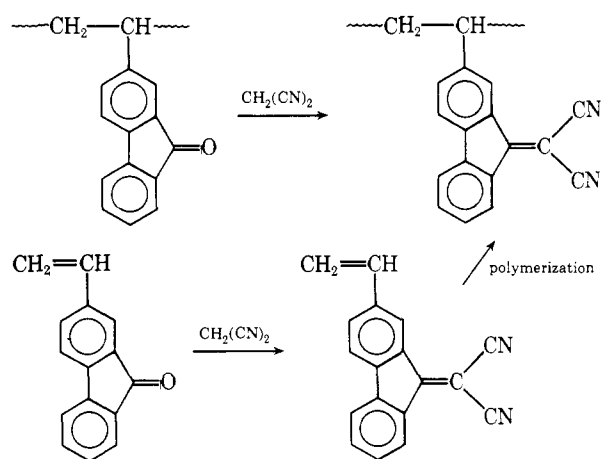
values are in the range 0.6 to 0.8, indicative of a random coil structure in these solvents. The \bar{M}_n and \bar{M}_w values can be determined from analysis of the gpc traces and correspond to chain extended molecular sizes based on polystyrene. The reliability of this method has been established for a number of vinyl aromatic polymers by Heller²⁰ and Sitaramaiah.²¹

Based on the solubility findings, the absence of any measurable insoluble materials in the polymer samples, and these molecular weight analyses it must be concluded that poly(2-vinylfluorenone) is a linear vinyl type polymer. It behaves as a typical vinyl aromatic polymer possessing a random coil configuration in some typical organic solvents.

Derivatives of Poly(2-vinylfluorenone). The carbonyl function in poly(2-vinylfluorenone) is amenable to chemistry and partial conversion into a number of novel derivatives was demonstrated, *e.g.*, reduction to the corresponding alcohol, conversion to an acetal, oxime, hydrazone,²² etc. All of these reactions were readily carried out using conventional reagents to low, <10%, conversion. Attempts to achieve higher conversions generally created solubility problems and no attempts were made to optimize the systems.

Fluorenone is known to react readily with malononitrile, $\text{CH}_2(\text{CN})_2$, to form 9-dicyanomethylenefluorene. Similarly treatment of 2-vinylfluorenone in methanol with malononitrile in the presence of piperidine gave a red/brown crystalline product, mp 213–215°, which was shown to be 2-vinyl-9-dicyanomethylenefluorene by spectroscopic and elemental analysis. This monomer is extremely insoluble and all attempts at free radical polymerization gave deep red insoluble polymeric products. The polymer poly(2-vinylfluorenone) also reacts to form the corresponding 9-dicyanomethylenefluorene derivative. Conversions higher than 50% resulted in formation of red, very poorly soluble, polymeric products. The copolymers containing less than approximately 50% of 2-vinyl-9-dicyanomethylenefluorene are yellow to red in color and are soluble in a number of common organic solvents.

One other interesting derivative of poly(2-vinylfluorenone) was investigated *i.e.*, a polymer containing diazofluorene functional groups. The preparation of this unique copolymer and its photochemistry are described in part II.²³ The photophysical and photochemical characteristics of poly(2-vinylfluorenone) are discussed in part III²² of this series.



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Preparation and Characterization of a Monodisperse, Semiflexible Polymer, Poly(*tert*-butyl crotonate)

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ABSTRACT: If *tert*-butyl crotonate monomer is highly purified, it can be polymerized by using an anionic initiator, 2-methylbutyllithium. The experimental conditions for polymerization are studied in detail. The polymerization proceeds without termination and the molecular weight distribution of the polymer becomes monodisperse over a wide range of molecular weight. The poly(*tert*-butyl crotonate) is soluble in various solvents and shows a feature of a semiflexible chain due to steric hindrance.

Study on the polymerization of crotonic ester, $\text{CH}_3\text{CH}=\text{CHCOOR}$ (R = alkyl group), is meaningful from various viewpoints. There are various unsolved problems in the polymerization mechanism of α,β -disubstituted mono-

mers, but, moreover, the polymers of crotonic esters are important in the physical chemistry of polymers. That is, they are useful for the study on configuration and conformation of ditactic polymers. The polymers of crotonic esters can