Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Lenz, Robert w.(1975) 'Ionic Polymerization of α, α -Disubstituted Vinyl Monomers', Journal of Macromolecular Science, Part A, 9: 6, 945 — 959

To link to this Article: DOI: 10.1080/00222337508081502

URL: http://dx.doi.org/10.1080/00222337508081502

J. MACROMOL. SCI.—CHEM., A9(6), pp. 945-959 (1975)

Ionic Polymerization of α,α-Disubstituted Vinyl Monomers

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ABSTRACT

Alkyl α-chloroacrylates and p-substituted α-methylstyrenes were investigated for the effect of polymerization conditions on tacticity, molecular weight, and distribution, and for the relationship between tacticity, glass temperature, and crystalline properties.

INTRODUCTION

The ionic polymerization reactions of substituted α-methylstyrenes and of α-chloroacrylate esters are under investigation in this laboratory for the effect of polymerization initiators and reaction conditions on tacticity and subsequently on physical properties. Unusually high stereoregularities have been obtained in some of these systems, and the control of molecular weight distribution has been a problem in many cases. The unsolved problems connected with these observations for the cationic polymerization of the α-methylstyrene monomers and the anionic polymerization of the α-chloroacrylate monomers, as well as for the ionic polymerization reactions of similar monomers, are discussed.

POLY(ALKYL α-CHLOROACRYLATES)

For the determination of the effect of tacticity on physical properties, it is necessary to be able to prepare polymers of varied stereochemical structures ranging from highly syndiotactic to highly isotactic in character [1]. In our earlier work on ethyl α-chloroacrylate, we attempted to prepare polymers of high syndiotacticity by homogeneous anionic and free-radical polymerization reactions, but it was observed that only relatively low molecular weight polymers were obtained in the former. The low molecular weights of these anionic polymers were always accompanied by a lower than theoretical chlorine analysis, and careful attempts have been made in the present investigations to eliminate the possible termination or transfer reactions which might be responsible for these two effects. Nevertheless, in spite of considerable effort and detailed investigations of a variety of homogeneous anionic systems, a few of which are listed in Table 1 for the three different ester monomers studied, it was not found possible to improve upon the molecular weights previously obtained, so that in almost all cases, number-average molecular weight values of less than 10,000 were obtained. On the other hand, free radical polymerization reactions were readily applicable to the preparation of syndiotactic polymers of high molecular weights for all three ester monomers as shown in Table 1.

Our attempts to prepare highly isotactic polymers in the previous investigations of the polymerization of ethyl α-chloroacrylate were concentrated on the use of Grignard-reagent initiators, which have been found to be very effective for this purpose in the polymerization of methyl methacrylate. Again in those investigations, only low molecular weight materials of atactic structures were obtained with these initiators. However, we were fortunate since that work because of the publication of a new catalyst system by Breslow and Kutner which was found by them and others to be very effective for the synthesis of isotactic polymers from both methyl methacrylate and α-chloroacrylate ester monomers [2, 3]. Their catalyst was obtained from the 1,4-addition reaction of a Grignard reagent to an unsaturated ketone. The solid product from this reaction was reported to be a very effective catalyst for the preparation of highly isotactic, high molecular weight crystalline polymers when used in a variety of

TABLE 1. Anionic and Free-Radical Polymerization of α-Chloroacrylate Esters

Monomer	Initiator[a]	Temp (°C)	Yield (%)	$\overline{M}_n$
Methyl α-chloroacrylate	n-BuLi	0	55	3,600
	t-BuLi	-78	45	4,300
	C_6H_5Li	-78	15	4,200
	C_6H_5Na	-78	1	4,800
	Bz_2O_2	70	90	270,000
	Benzoin-UV	-50	60	109,000
Ethyl α-chloroacrylate	n-BuLi	-78	16	6,000
	n-BuLi	0	25	4,500
	FLi	-78	9	5,000
	Bz_2O_2	70	90	362,000
	Benzoin-UV	-50	12	181,000
Isopropyl α-chloroacrylate	n-BuLi	-78	51	8,000
	Bz_2O_2	60	54	77,300
	Benzoin-UV	-65	5	2,100

[a] Anionic polymerization reactions were run in toluene; Bz_2O_2 is benzoyl peroxide, FLi is fluorenyl lithium.

solvents such as ethers, aliphatic and cyclic hydrocarbons, and aromatic hydrocarbons over a wide range of temperatures, from -60 to 100°C. These heterogeneous initiators were also applied to the polymerization of methyl, ethyl, and isopropyl α-chloroacrylate with the results shown in Table 2 for some of the products obtained.

The products of all polymerization reactions, in which molecular weights above 10,000 were obtained, were characterized for tacticity as fully as possible by IR and NMR spectroscopy and for glass transition temperature and crystalline properties by DSC. For complete tacticity analysis, both 100 and 300 MHz proton magnetic resonance spectroscopy were used for the determination of triad and tetrad structures of each of the three poly(alkyl α-chloroacrylates), and it was found possible to make assignments and carry out quantitative analyses for all of the tetrad peaks in the backbone methylene resonance of methyl, ethyl, and isopropyl ester polymers of syndiotactic atactic and isotactic structures. Representative tetrad spectra for the ethyl ester polymers are shown in Fig. 1.

In addition, the methyl singlet peaks of poly(methyl α-chloroacrylate), the methyl triplet peaks of poly(ethyl α-chloroacrylate), which had not been amenable previously to resolution at 220 MHz, and the methyl doublet peaks in poly(isopropyl α-chloroacrylate) were resolved. The latter are shown in Fig. 2 for isopropyl ester polymers of different tacticities. The triad values which were obtained from these pendant ester group resonances compared favorably with triad values

TABLE 2. Polymerization of α-Chloroacrylate Esters with Heterogeneous Grignard-Based Catalyst

Monomer	Monomer to catalyst ratio	Yield (%)[a]	$\overline{M}_n$
Methyl α-chloroacrylate	55	11	13,000
	150	25	32,000
	160	10	42,000
	300	5	10,600
Ethyl α-chloroacrylate	150	12	309,000
Isopropyl chloroacrylate	100	5	50,000

[a] At 30°C for 18 to 20 hr reaction time.

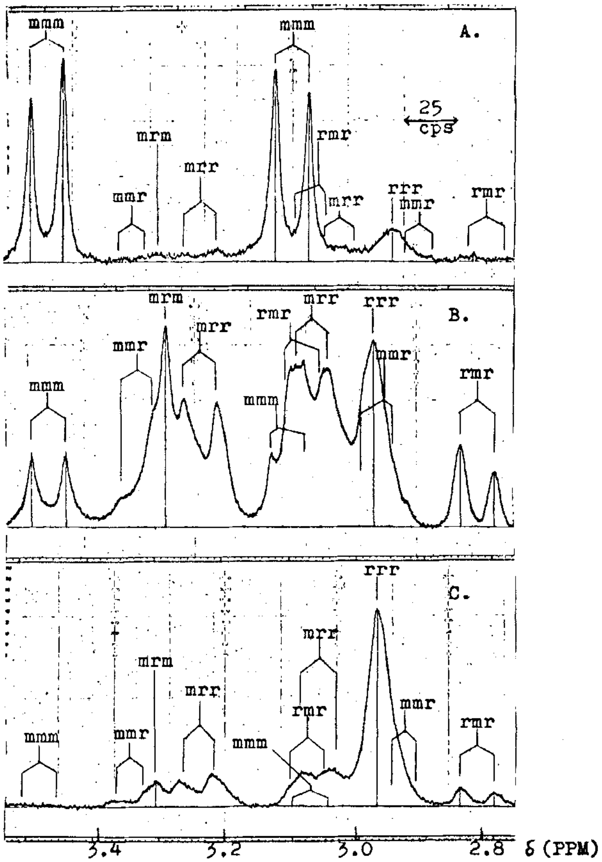


FIG. 1. Methylene proton region of 300 MHz spectra of poly(ethyl α-chloroacrylate). (A) Isotactic, (B) heterotactic, and (C) syndiotactic polymers.

calculated from experimental tetrad values as shown in Table 3 for representative samples of the isotactic ethyl ester polymers.

For mechanism interpretations, and also as an additional demonstration of the internal agreement of the triad and tetrad peak assignments, statistical calculations of the expected triad and tetrad structures of all atactic and syndiotactic polymers, which were prepared by either homogeneous anionic or free-radical polymerization, were made on the basis of random selection or Bernoullian statistics with

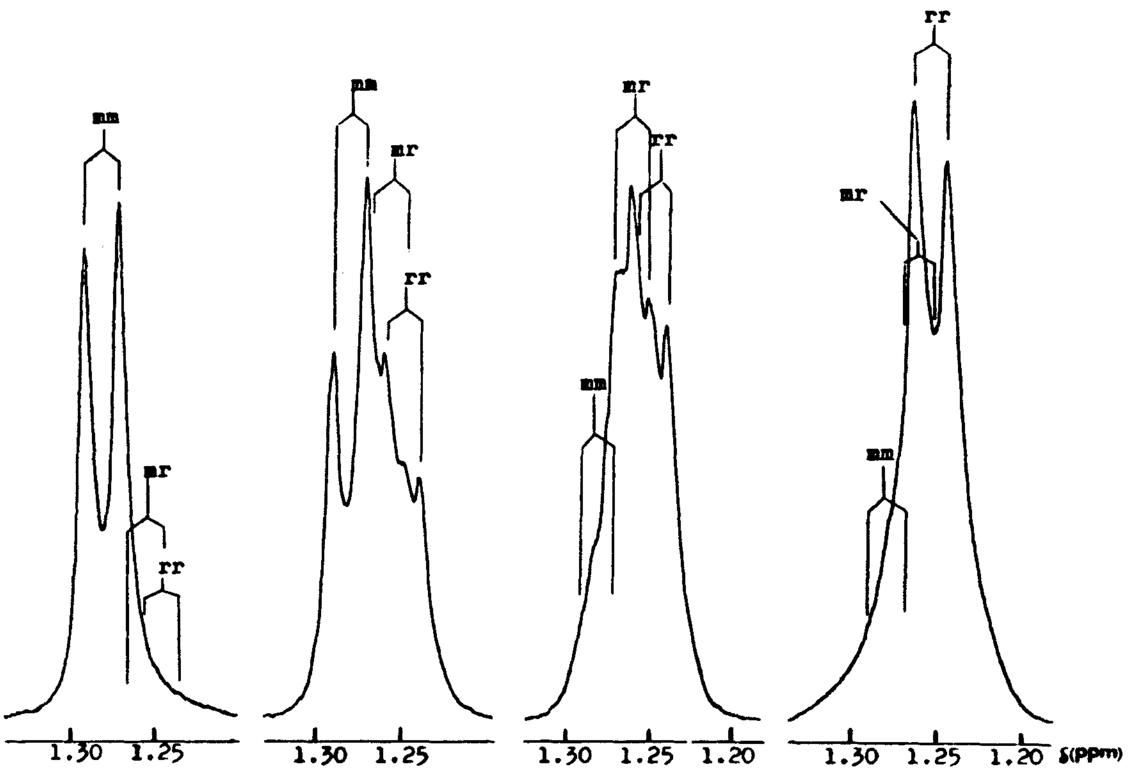


FIG. 2. Isopropoxy methyl region of 300 MHz spectra of poly(isopropyl α-chloroacrylate). Left to right: isotactic, moderately isotactic, heterotactic, and syndiotactic polymers.

TABLE 3. Observed and Calculated Triad Tacticities of Isotactic Poly(ethyl α-Chloroacrylate)

Polymer sample	Triad	Triad amounts: Observed from ethoxy-methyl resonance	Triad amounts: Calculated from methylene tetrads
1	mm	0.814	0.798
	mr	0.083	0.082
	rr	0.103	0.120
2	mm	0.650	0.678
	mr	0.125	0.112
	rr	0.225	0.210

the results collected in Table 4. Many, but not all, of these polymers were found to adhere very closely to this type of propagation statistics, and those that did are so indicated in the results collected in Table 4. Surprisingly, the free-radical polymerization of the methyl and isopropyl monomers did not yield Bernoullian polymers. For reasons not yet obvious, these polymers had tetrad distributions more closely described by first-order Markov statistics.

In contrast, the tetrad distributions of the moderately to highly isotactic polymers prepared with the Breslow-Kutner catalyst were found to be consistent with a nonrandom propagation process as revealed by their agreement with values calculated on the basis of first-order Markov statistics as shown in Table 5. From the general tacticity results and the implications of the first-order Markov statistics, coupled with other tacticity information, especially the large amounts of mrr and rrr triads present, it seems likely that the isotactic stereoregularity obtained with the Breslow-Kutner catalyst is attributable primarily to a competition between "template" and end-group control of the insertion reaction. That is, the isotactic stereoregulation is caused by the asymmetry of the active site of the catalyst, which must counteract a strong tendency toward syndiotactic placement by the end groups. According to this interpretation, the mrr tetrad results from an attempt by the catalyst to restore the proper absolute configuration to the chain end after a propagation mistake is made, and the mrm tetrads which would occur under conditions of isotactic "steric" control by the end

TABLE 4. Triad and Tetrad Information for Anionic and Free-Radical Polymers Assumed to Follow Bernoullian Growth Statistics

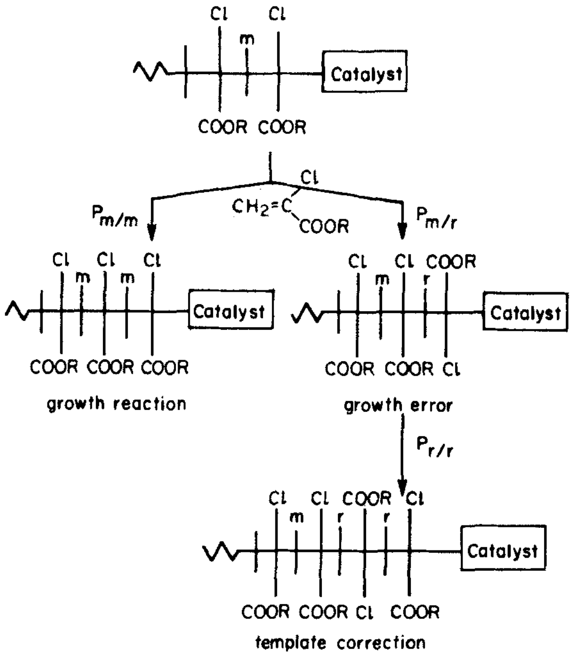
Polymer type and initiation	P_m[a]	Bernoullian statistics	Triads			Tetrads					
			mm	mr	rr	mmm	mmr	rmr	mrm	mrr	rrr
Methyl ester,[b] anionic	0.40	Obs	0.17	0.49	0.34	0.07	0.19	0.16	0.11	0.27	0.20
		Calc	0.16	0.49	0.35	0.07	0.19	0.14	0.10	0.29	0.21
Methyl ester,[c] free-radical	0.30	Obs	0.12	0.35	0.53	0.05	0.14	0.11	0.05	0.23	0.42
		Calc	0.09	0.41	0.50	0.03	0.12	0.15	0.06	0.29	0.35
Ethyl ester,[b] anionic	0.46	Obs	0.21	0.49	0.30	0.13	0.16	0.15	0.11	0.29	0.16
		Calc	0.21	0.49	0.30	0.09	0.23	0.14	0.11	0.27	0.16
Ethyl ester,[b] free radical	0.20	Obs	0.05	0.29	0.66	0.02	0.06	0.11	0.03	0.23	0.55
		Calc	0.04	0.31	0.65	0.01	0.06	0.13	0.03	0.25	0.52
Isopropyl ester,[c] free radical	0.26	Obs	0.14	0.44	0.42	0.04	0.20	0.13	0.10	0.23	0.30
		Calc	0.07	0.38	0.55	0.02	0.10	0.14	0.05	0.29	0.40

[a] Calculated from observed tetrad tacticity.
[b] Good agreement between observed and calculated tacticities.
[c] Poor agreement between observed and calculated tacticities.

TABLE 5. Observed and Calculated First-Order Markov Tetrad Amounts for Isotactic Poly(alkyl α-Chloroacrylates)

		Tetrads[a]					
Polymer type	Statistics	mmm	mmr	rmr	mrm	mrr	rrr
Methyl ester	Obs	0.56	0.09	0.07	0.04	0.12	0.12
	Calc	0.51	0.17	0.02	0.04	0.14	0.12
Ethyl ester	Obs	0.79	0.02	0.03	0.01	0.07	0.08
	Calc	0.76	0.08	0.00	0.01	0.06	0.09
Isopropyl ester	Obs	0.92	0.01	0.02	0.01	0.04	0.01
	Calc	0.92	0.05	0.00	0.01	0.02	0.01

groups are not present to any extent. Therefore the principal propagation sequence involving an error and its subsequent correction can be represented as shown by Scheme 1.



SCHEME 1.

POLY-α-METHYLSTYRENES

Cationic polymerization reactions of α-methylstyrene are known to give predominantly syndiotactic polymers [4]. We were interested to learn how this stereoregularity depends upon monomer structure and polymerization conditions, specifically counterion and solvent, and how it affects crystallinity of the polymers. For this purpose we polymerized a series of p-substituted-α-methylstyrene monomers at -78°C using various Friedel-Crafts initiators and solvents. In the initial investigations, unsubstituted, p-methyl- and p-chloro-α-methylstyrene were polymerized and polymer tacticities were determined by NMR spectroscopy. The α-methyl peaks were used for quantitative tacticity analyses in all cases, but for the p-chloro polymers the phenyl proton peaks could also be used. Typical spectra for p-chloro-α-methylstyrene polymers of high and intermediate syndiotacticities are shown in Fig. 3.

For all three monomers, solvent polarity was found to have a strong influence on tacticity, and polar solvents favored the formation of highly syndiotactic polymers (up to 96%) as shown in Table 6. The influence of initiator was of less importance in polar solvents, but it was quite appreciable in hexane (for example, 67% syndiotactic content for boron trifluoride etherate compared to 90% for boron trifluoride, see Table 6). As expected, samples of the same polymer but with different tacticity showed reasonably good correlation between stereoregularity and crystallinity as shown in Table 6. Thus the two polymers of highest content of syndiotactic triads in the p-methyl series had sufficiently high degrees of crystallinity for detection by x ray. The p-chloro polymers showed crystalline melting points in all cases except when the stereoregularity was very low. The melting points varied with tacticity roughly as expected, but the glass transition temperatures showed the expected variations only for the p-methyl polymers as shown in Table 6. In sharp contrast to the crystallinities of the p-methyl and p-chloro polymers, the unsubstituted polymer lacked crystallinity even at 92% syndiotactic content. This strong effect of p-substituent on crystallinity may depend on either a thermodynamic or kinetic ability of certain substituents to facilitate the crystallization process of such polymers. As the T_g/T_m ratios within this series of poly-α-methylstyrenes is unusually high (0.8 to 0.9), it is perhaps not surprising that their ability to crystallize is quite sensitive to structural variations.

As to the tacticity results of Table 6, polymerization conditions and monomer structure undoubtedly affect the nature of the growing ion-pair and thereby the steric course of the propagation reaction in

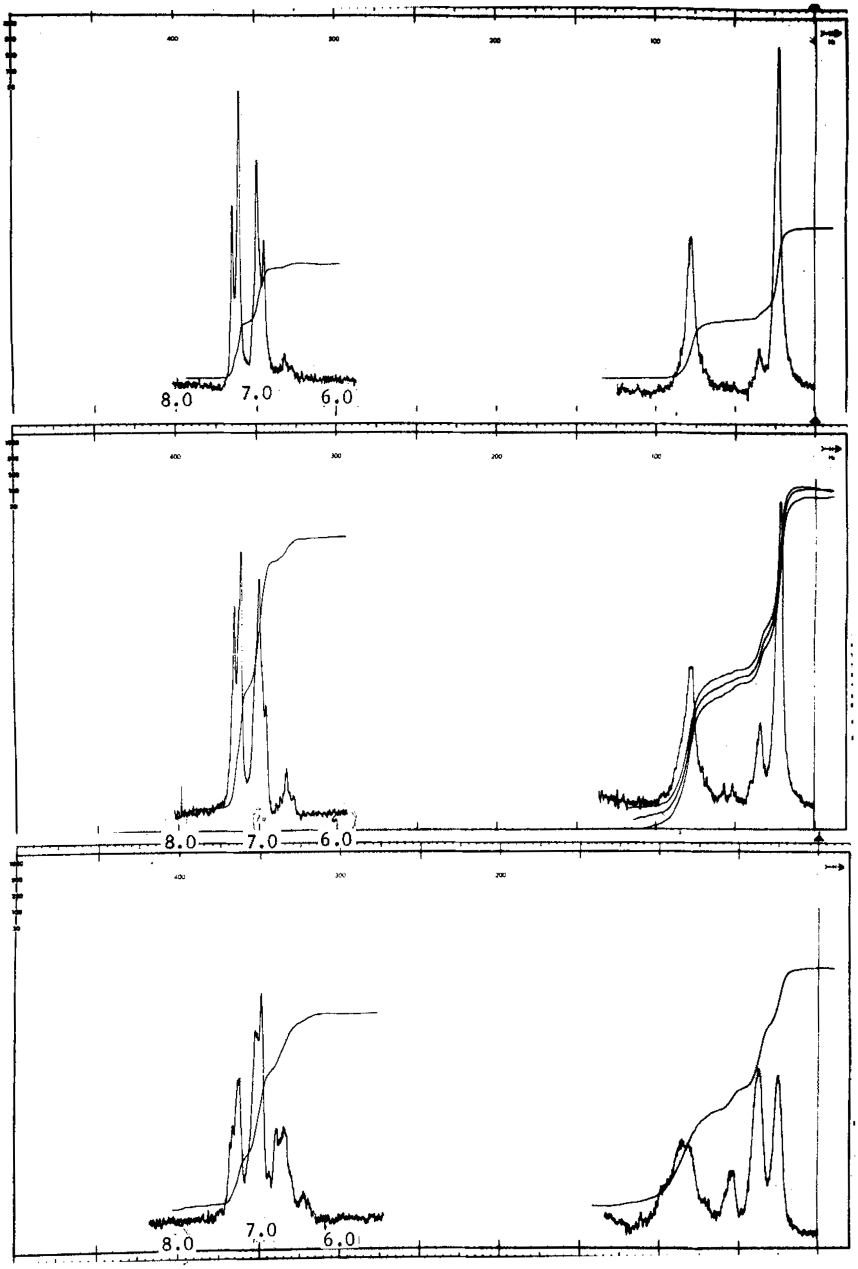


FIG. 3. 100 MHz NMR spectra of poly-p-chloro-α-methylstyrene. Top to bottom: 90, 79, and 40% syndiotactic triad contents.

TABLE 6. Effect of Polymerization Conditions on Structure and Properties of α-Methylstyrene Polymers[a]

Monomer: p-substituent	Initiator	Solvent[b]	Triad tacticity (%)			Properties	
			S	H	I	T_g (°C)	T_m (°C)
H	$TiCl_4$	M	92	6	2	180	none
	$BF_3 \cdot OEt_2$	H/C[d]	81	19	0	-	-
	BF_3	H/C[d]	84	16	0	-	-
	BF_3	T	88	12	0	-	-
	BF_3	H	57	32	11	-	-
CH_3	$BF_3 \cdot OEt_2$	H/C[d]	94	6	0	175	225
	$BF_3 \cdot OEt_2$	T	96	4	0	176	217
	$BF_3 \cdot OEt_2$	H	67	24	9	165	204
	BF_3	H	90	10	0	-	-
Cl	$TiCl_4$	M	83	13	4	143	214
	$TiCl_4$	M/T[d]	79	19	2	151	209
	$TiCl_4$	M/H[d]	76	21	3	-	-
	$TiCl_4$	T	71	25	4	154	209
	$TiCl_4$	H	42	48	10	153	-
	$AlCl_3$	M	90	10	0	133	213
	BF_3	M	79	19	2	-	-
	$SnCl_4$	M	85	13	2	-	-

[a] All polymerization reactions were run at -78°C.
[b] M, methylene chloride; H, hexane; C, chloroform; T, toluene.
[c] S, syndiotactic triads; H, heterotactic triads; I, isotactic triads.
[d] Solvent mixture.

these polymerizations. The more polar the solvent, presumably the more separated is the counterion from the growing cation, and the syndiotactic product, which has the least steric crowding, should be formed [5]. In a nonpolar solvent a tighter ion-pair, and even a coordinate covalent structure, is possible in the propagation step, which could be more like a substitution reaction so that the sterically-strained heterotactic or isotactic sequence becomes possible [5]. Hence the products of these reactions are less stereoregular, and the lower melting points and glass transition temperatures are a result of lower syndiotactic contents. For these reasons the steric course of the propagation reaction was found to be more sensitive to change of initiator, and thus counterion structure, in nonpolar solvents than in polar ones.

Electron-donating p-substituents operating either through resonance interaction or on demand in the transition state of the addition reaction were expected to favor the formation of syndiotactic polymer by loosening the ion-pair structure, and such was the case as shown in Table 7 for a wide variety of substituted α-methylstyrene monomers. However, because all of these polymerization reactions were conducted in a highly polar solvent (methylene chloride) and ion-pair separation was apparently already large even in the unsubstituted case, electron-

TABLE 7. Tacticity and Molecular Weight as a Function of Para-Substituent in α-Methylstyrene Polymers[a]

Polymer: p-substituent	Triad tacticity (%)[b] S	H	I	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$
H	92	6	2	41	145
CH_3	95	5	0	-	-
$CH(CH_3)_2$	85	10	5	22	51
$C(CH_3)_3$	85	14	1	15	50
OCH_3	91	7	2	32	85
Cl	83	13	4	171	405
F	83	17	0	247	984
CF_3	45	45	10	43	102

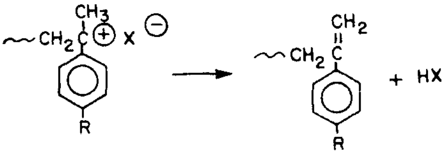
[a] All polymers were prepared in methylene chloride at -78°C with $TiCl_4$ catalyst.

[b] See Table 6 for abbreviations.

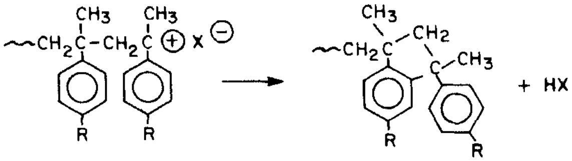
donating groups brought about only relative small increases in syndiotactic content.

Polar solvents favored the formation of higher molecular weight polymers, and among the initiators evaluated, stannic chloride gave the highest molecular weight of all. When sufficiently small amounts of titanium tetrachloride or aluminum chloride initiators were used, 0.2 mole %, the polymer obtained showed a single peak on GPC. Larger amounts of initiator, 1%, resulted in polymers with a binodal molecular weight distribution, and the stereoregularity of the low molecular weight fraction was found to be somewhat inferior to that of the high molecular weight fraction (72 compared to 83%, respectively, of syndiotactic triads). Electron-withdrawing substituents like chloro and fluoro groups also seemed to favor the formation of higher molecular weight polymers.

The solvent effect on molecular weight can again be rationalized on the basis of the termination reaction mechanism as a function of end-group ion-pair structure. Tighter ion-pair end-groups in nonpolar solvent could conceivably show enhanced counterion chain transfer, in competition with normal propagation:



On the other hand, the substituent effect would be consistent with an intramolecular alkylation, chain transfer reaction of the type.



That is, electron-withdrawing substituents would be expected to deactivate the aromatic ring to this type of alkylation reaction, thereby enhancing the relative role of propagation and polymer chain length. The relative contributions of these two molecular termination reactions, and the existence of a binodal molecular weight distribution and higher initiator amounts, remain unsolved problems in this and other closely related cationic polymerization reactions [6].

ACKNOWLEDGEMENTS

The work described in this review involved the contributions of many of the author's associates at the University of Massachusetts and elsewhere. The α-chloroacrylate investigations were carried out by Dr. Gerald Dever [7] (present address: Research Laboratories, Xerox Corporation, Rochester, New York) under the codirection of Professors William MacKnight and Frank Karasz of our Polymer Science and Engineering Program and Materials Research Laboratory. The α-methylstyrene investigations were carried out by Dr. Judith Sutherland [8] (present address: Research Laboratories, Eastman Kodak Co., Rochester, New York) and Dr. Lars Westfelt (present address: Chemistry Department, Swedish Forest Products Research Laboratory, Stockholm, Sweden). In addition, NMR investigations on p-fluoro-α-methylstyrene were made in collaboration with Dr. W. Regel of the Institute of Macromolecular Chemistry at the University of Freiburg in Germany [9]. The financial support of the National Science Foundation which permitted the presentation of this paper is gratefully acknowledged.

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