Polymerization of Methyl Methacrylate by Alkali Metal Compounds

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Abstract:

The structure of poly(methyl methacrylate) prepared by anionic polymerization was followed. Compounds of lithium, sodium, and potassium were used as initiators. The influence of the structure of the initiator and its amount and of the monomer concentration, conversion, and temperature on the structure of the polymer in the polymerization without the presence of complexing solvents was studied. By analysis of NMR spectra tacticity and stereoblock structure, characterized by the parameter $\eta = p_{is}/(p_{is}+p_{ss})$ was determined. The results made possible the conclusions concerning the factors controlling the growth reaction.

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Synopsis

The structure of poly(methyl methacrylate) prepared by anionic polymerization was followed. Compounds of lithium, sodium, and potassium were used as initiators. The influence of the structure of the initiator and its amount and of the monomer concentration, conversion, and temperature on the structure of the polymer in the polymerization without the presence of complexing solvents was studied. By analysis of NMR spectra tacticity and stereoblock structure, characterized by the parameter $\eta = p_{is}/(p_{is} + p_{ss})$, was determined. The results made possible the conclusions concerning the factors controlling the growth reaction.

Introduction

The relations between methyl methacrylate polymerization conditions and the stereoregularity of the polymer are relatively well known. A systematic study of the influence and mutual relations of various factors, leading to conclusions of a more general type, has so far been restricted to compounds of lithium.[1] Even in this case the sequence distribution of isotactic and syndiotactic diads has not been determined.

In the present communication the stereoregularity of poly(methyl methacrylate), prepared with alkali metal compounds under well-defined polymerization conditions,[2] is investigated in detail. The influence of type and amount of initiator, and degree of conversion, temperature, and concentration of monomer were followed. To avoid complications, only a nonpolar solvent was used. Where tetrahydrofuran had to be used, its amount was restricted to the minimum necessary for the dissolution of the initiator. For comparison the influence of tetrahydrofuran on sodium-initiated and potassium-initiated polymerization was shown. The distribution of stereoregular sequences in the polymer was followed by means of NMR.

Bovey and Tiers[3] have shown that NMR spectra of poly(methyl methacrylate) exhibit three bands at τ equal to 8.78, 8.95, and 9.09, corresponding to methyl groups in isotactic "ii," heterotactic "is," and syndiotactic "ss" triads; the contents of isotactic "i" and syndiotactic "s" diads (tacticity) can easily be obtained from their relative intensities. It also follows from this work that the sequence distribution of isotactic and

syndiotactic diads in the polymer cannot be expressed as a simple function of tacticity. We therefore sought a different way of describing the sequence distribution of diads.

Theoretical

Let us assume that the probabilities of syndiotactic or isotactic placement of a monomer unit are functions of the configuration of the ultimate diad only, and let us designate them by the symbols p_{ii}, p_{is}, p_{ss}, p_{si}. Respecting the relations $p_{is} + p_{ii} = 1$, $p_{ss} + p_{si} = 1$ only two of these values, designated further by α and β, are independent:

$$\alpha = p_{ss}, \qquad \beta = p_{is}, \qquad p_{ii} = 1 - \beta, \qquad p_{si} = 1 - \alpha$$

The complete sequence distribution of the polymer can in this case be described by the values of α and β. Let us designate the probability of occurrence of a sequence with a given configuration by $P(i)$, $P(s)$, $P(ii)$, ... The relations for the probabilities of the diads "i" and "s" may then be obtained from the equations

$$P(s)\alpha + P(i)\beta = P(s), \qquad P(i)(1 - \beta) + P(s)(1 - \alpha) = P(i) \quad (1a)$$

from which

$$P(i) = (1 - \alpha)/(1 + \beta - \alpha), \qquad P(s) = \beta/(1 + \beta - \alpha) \qquad (1b)$$

For triads we have:

$$S = P(ss) = P(s)\alpha = \alpha\beta/(1 + \beta - \alpha)$$
$$H = P(si) + P(is) = P(s)(1 - \alpha) + P(i)\beta = 2\beta(1 - \alpha)/(1 + \beta - \alpha)$$
$$I = P(ii) = P(i)(1 - \beta) = (1 - \alpha)(1 - \beta)/(1 + \beta - \alpha) \qquad (2)$$

Tetrad characteristics may be calculated in a similar way. The resulting expressions are summarized in Table I. Now

$$\alpha = p_{ss} = 2/(2 + H/S), \qquad \beta = p_{is} = (H/I)/(2 + H/I) \qquad (3)$$

Since the values of S, H, and I are proportional to the intensities of the three CH_3 bands, the determination of the parameters α and β is straightforward. To verify whether the growth of poly(methyl methacrylate) can be fully described by means of the parameters α and β an analysis of the CH_2 band in the NMR spectra of poly(methyl methacrylate) was performed; as mentioned by Bovey,[4] in analogy to other vinyl polymers the structure of the CH_2 band is expected to be sensitive to tetrad characteristic. Numerical analysis has actually shown that an interpretation of the CH_2 band (Table I) can be found that is consistent with expressions for tetrad distribution (Table I) in a very broad range of tacticity and block-character values (Fig. 1, Table II). The sequence distribution of a polymer conforming to this assumption may be characterized by a point in a square with coordinates α and β (Figs. 2 and 3). For a statistical polymer $p_{is} = p_{ss}$; statistical polymers therefore lie on the diagonal $\alpha = \beta$. The heterotacticity index $\eta = p_{is}/(p_{is} + p_{ss})$ has been introduced by some

TABLE I

Probability of Occurrence of Various Tetrad Sequences and Interpretation of the CH₂ Band[a]

Tetrad	Probability of occurrence	Type of multiplet	AB shift, cps	J_{AB}	Frequencies and intensities of multiplet components			
iii	$\dfrac{(1-\alpha)(1-\beta)^2}{1+\beta-\alpha}$	quartet	40.3	15	83 (0.166)	98 (0.334)	126 (0.334)	141 (0.166)
iis	$\dfrac{2(1-\alpha)(1-\beta)\beta}{1+\beta-\alpha}$	quartet	38.2	15	79.6 (0.160)	94.6 (0.342)	120.6 (0.342)	135.6 (0.160)
sis	$\dfrac{(1-\alpha)\beta^2}{1+\beta-\alpha}$	quartet	40.3	15	83 (0.166)	98 (0.334)	126 (0.334)	141 (0.166)
isi	$\dfrac{\beta(1-\alpha)^2}{1+\beta-\alpha}$	singlet	—	—		118.6		
iss	$\dfrac{2\alpha\beta(1-\alpha)}{1+\beta-\alpha}$	quartet	6.1	15	99.2 (0.016)	114.2 (0.484)	115.4 (0.484)	130.4 (0.016)
sss	$\dfrac{\beta\alpha^2}{1+\beta-\alpha}$	singlet	—	—		111		

[a] Frequencies are given in cps from hexamethyldisiloxane HMDS at 60 Mc.

TABLE II
Parameters of Poly(methyl Methacrylate) Samples Shown in Figure 1

Sample	$S, \%$	$H, \%$	$I, \%$	$P(s), \%$	α	β	η
A53	41	29	30	56	0.74	0.33	0.31
A81	25	32	43	41	0.61	0.27	0.31
A22	15	26	59	28	0.54	0.18	0.25
A42	7	14	79	14	0.50	0.08	0.14
682[a]	75	22	3	86	0.87	0.79	0.48
A8[a]	27	52	21	53	0.51	0.55	0.52

[a] Sample does not belong in the series investigated.

authors;[5] in our case the block character (or "disordering") of the polymer is fully characterized by this index. Polymers with an equal block character of $\eta = $ const. in our plot lie on straight lines passing through the origin.

Polymers of equal tacticity lie in our plot on straight lines passing through the point $(\alpha = 1, \beta = 0)$:

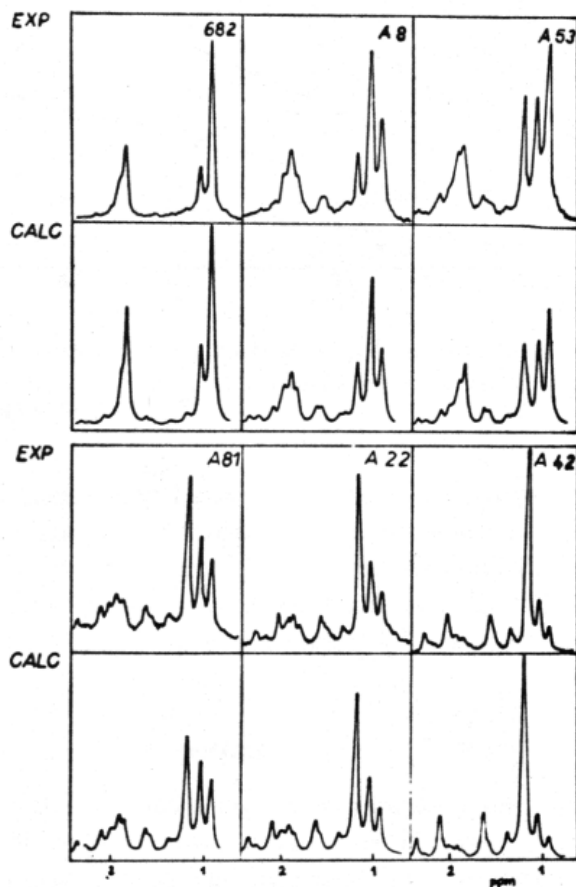$$P(s)/P(i) = k = \text{const.} \rightarrow \beta = k(1 - \alpha)$$

Fig. 1. Experimental and theoretical spectra of poly(methyl methacrylate). Sample parameters are given in Table II. Half-bandwidth 33 cps was used for calculation.
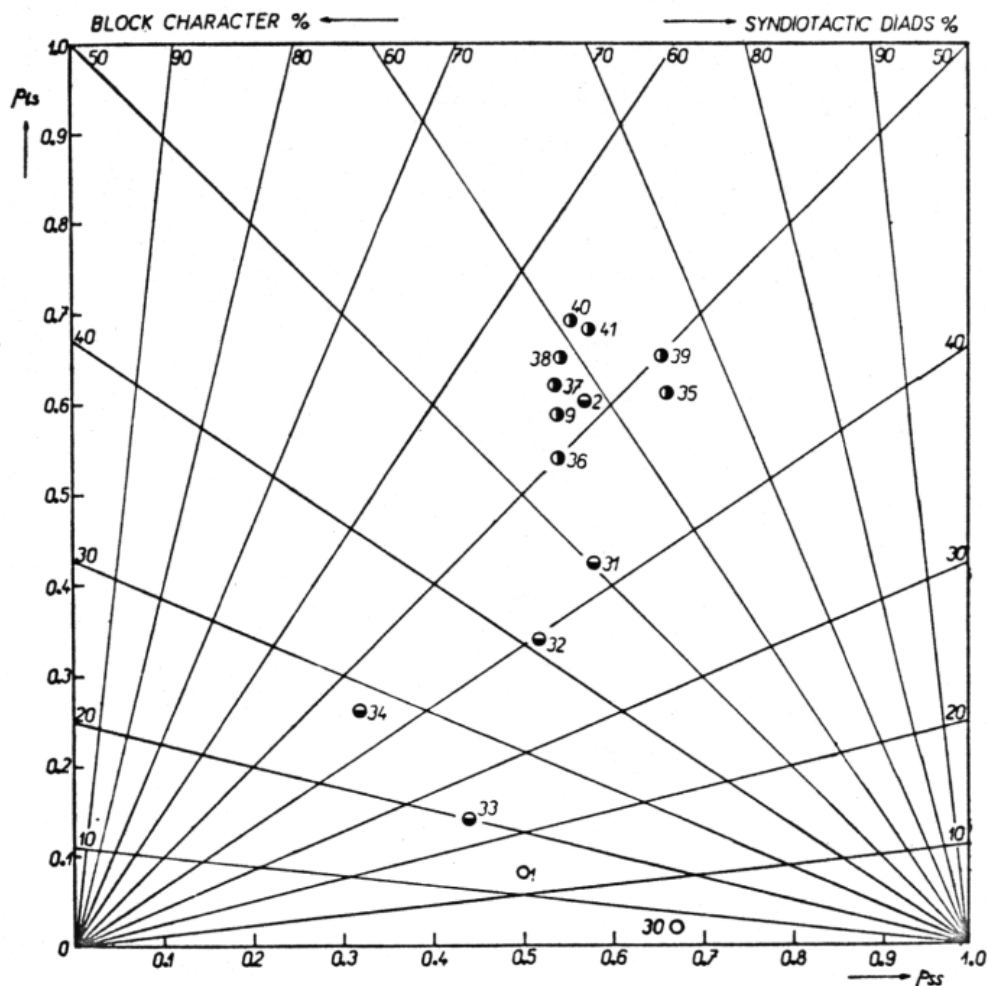
Fig. 2. Dependence of stereoregular structure of poly(methyl methacrylate) polymerized by alkoxides of Li, Na, and K at various temperatures: (○) BuOLi, (◐) t-BuONa, (◑) t-BuOK, (●) t-BuLi.

Polymers with equal mean lengths of purely isotactic and purely syndiotactic sequences lie in the plot on horizontal (β = const.) or vertical (α = const.) lines, respectively. The graphical representation in the coordinate frame (α, β) is therefore more convenient than, say, Bovey's triangular plots, in which all the above-mentioned straight lines are represented by curves.

Experimental

The preparation of the initiators used has been described in a previous communication.[2] The experimental setup was likewise identical. The initiator was continuously introduced into the thermostated monomer by means of equipment making possible an isothermal process at varying temperatures up to medium degrees of conversion. When the required degree of conversion was attained, polymerization was stopped by acetic
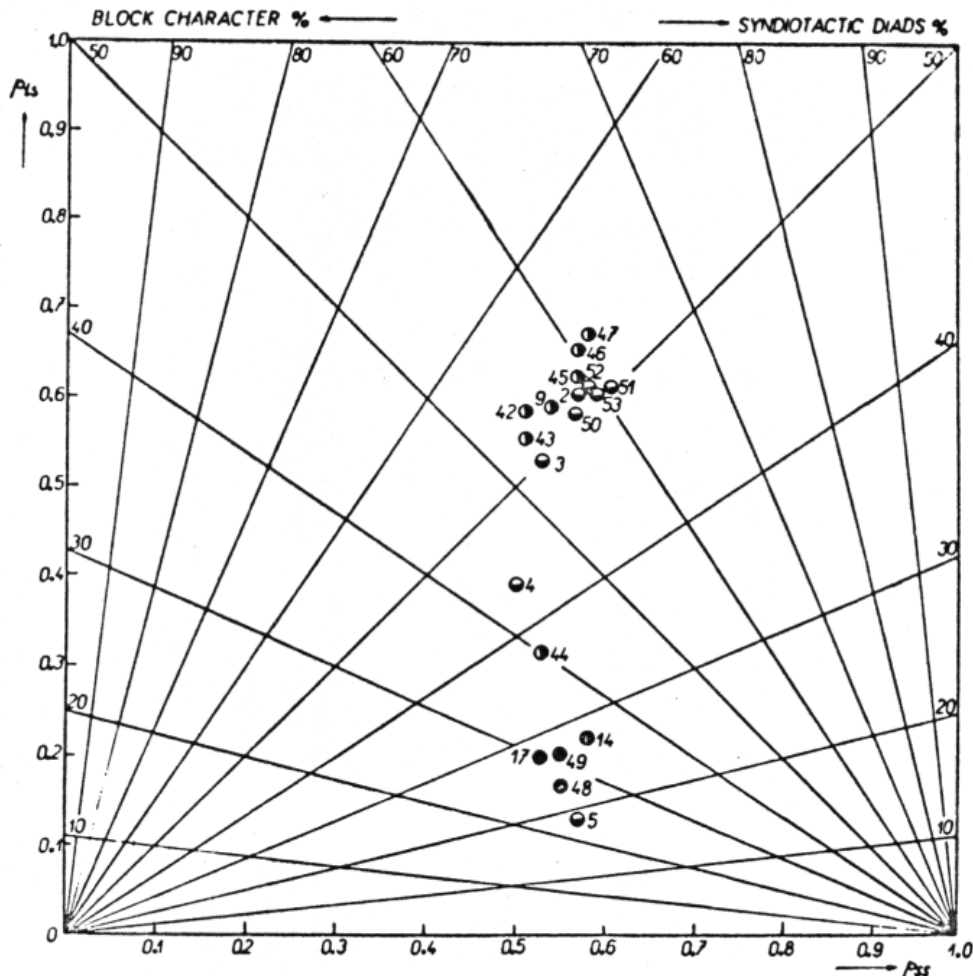
Fig. 3. Dependence of stereoregular structure of poly(methyl methacrylate) polymerized by compounds of Li, Na, and K at 20°C. on monomer concentration: (◒) *t*-BuONa, (◖) *t*-BuOK, (●) *t*-BuLi.

acid, and the polymer was precipitated into hexane, reprecipitated, and dried to constant weight. With alkyl-lithium initiators under the same polymerization conditions at low temperatures the polymer solution attained gel character at a conversion of several hundredths; investigation of the influence of degree of conversion on stereoregularity at low temperatures was made impossible by this circumstance.

The spectra of the investigated samples of poly(methyl methacrylate) were measured on the JNM-3-60 spectrometer at 60 Mc. Polymer solutions of 15% in a mixture of perchloroethylene and *o*-dichlorobenzene,[6] with HMDS as internal standard, were measured at 140°C.

Results and Discussion

Data characterizing the polymerization conditions of the samples investigated and the results of structure determination are summarized in Tables

TABLE III

Bulk Polymerization of Methyl Methacrylate by Alkoxides of Li, Na, and K at Various Temperatures

Exp. no.	Temp., °C.	Initiator	Initiator concn., mole/liter	Total amt. initiator added, moles	Convsn., %	I, %	H, %	S, %	p_{ss}	p_{is}
1	20	t-BuOLi	0.194	1.74×10^{-3}	3.39	79	14	7	0.50	0.08
30	-40	t-BuOLi	0.210	1.53×10^{-3}	4.52	95	3	2	0.67	0.02
2	20	t-BuONa	0.028	2.11×10^{-4}	14.92	17	50	33	0.57	0.60
31	-3	t-BuONa	0.137	6.37×10^{-4}	14.07	29	42	29	0.58	0.42
32	-10	t-BuONa	0.136	1.37×10^{-3}	16.55	39	40	21	0.52	0.34
33	-20	t-BuONa	0.072	1.11×10^{-3}	1.33	68	23	9	0.44	0.14
34	-30	t-BuONa	0.064	2.20×10^{-3}	1.32	53	38	9	0.32	0.26
35	80	t-BuOK	0.031	3.69×10^{-4}	15.74	14	43	43	0.67	0.61
36	60	t-BuOK	0.031	6.15×10^{-4}	17.13	21	50	29	0.54	0.54
37	40	t-BuOK	0.044	5.62×10^{-4}	3.69	16	53	31	0.54	0.62
9	20	t-BuOK	0.081	4.24×10^{-4}	11.66	18	52	30	0.54	0.59
38	-3	t-BuOK	0.055	4.23×10^{-4}	9.39	14	53	33	0.55	0.65
39	-10	t-BuOK	0.040	4.86×10^{-4}	7.84	14	51	25	0.64	0.65
40	-20	t-BuOK	0.035	4.03×10^{-4}	16.06	12	53	35	0.57	0.69
41	-30	t-BuOK	0.072	3.55×10^{-4}	14.03	12	52	36	0.58	0.68

TABLE IV

Polymerization of Methyl Methacrylate by Compounds of Li, Na, and K in Solutions at 20°C.

Exp. no.	Initiator	Initiator concn. mole/liter	Total amt. initiator added, moles $\times 10^3$	Solvent	Monomer concn. mole/liter	Convsn., %	I, %	H, %	S, %	p_{ss}	p_{sa}
14	t-BuLi	0.170	1.32	benzene	9.35	15.57	51	29	20	0.58	0.22
48	t-BuLi	0.148	0.995	benzene	4.67	8.15	60	25	15	0.55	0.17
17	t-BuLi	0.181	1.05	benzene	3.75	12.76	56	28	16	0.53	0.20
49	t-BuLi	0.148	0.765	benzene	0.467	22.30	55	28	17	0.55	0.20
2	t-BuONa	0.028	0.211	benzene	9.35	14.92	17	50	33	0.57	0.60
3	t-BuONa	0.033	0.089	benzene	7.61	15.35	22	50	28	0.53	0.53
4	t-BuONa	0.027	0.217	benzene	3.23	18.99	34	44	22	0.50	0.39
5	t-BuONa	0.033	0.242	benzene	1.81	2.86	67	20	13	0.57	0.13
50	t-BuONa	0.025	0.540	THF	7.48	8.88	18	49	33	0.57	0.58
51	t-BuONa	0.042	0.376	THF	5.61	17.91	17	49	34	0.58	0.59
52	t-BuONa	0.032	0.525	THF	3.74	19.37	15	50	35	0.58	0.61
53	t-BuONa	0.024	0.470	THF	1.87	72.93	16	49	35	0.59	0.60
9	t-BuOK	0.081	0.424	benzene	9.35	11.66	18	52	30	0.54	0.59
42	t-BuOK	0.048	0.541	benzene	7.48	5.27	19	53	28	0.51	0.58
43	t-BuOK	0.100	0.142	benzene	3.74	25.73	21	52	27	0.51	0.55
44	t-BuOK	0.098	1.596	benzene	1.87	42.50	42	37	21	0.53	0.31
45	t-BuOK	0.088	0.491	THF	7.48	9.35	15	51	34	0.57	0.62
46	t-BuOK	0.087	0.833	THF	1.87	35.97	14	52	34	0.57	0.65
47	t-BuOK	0.072	1.025	THF	0.467	60.14	12	52	36	0.58	0.67

III and IV.   The dependence of stereoregular structure on polymeriza-tion conditions is shown in Figures 2 and 3.

The complexing character of initiation is outstanding in the case of *t*-BuOLi, the greater part of which is transformed to primary alkoxide by re-esterification.   The character of the polymer prepared at larger concen-trations of alkyl-lithium is similar.   Both the stereoregularity of the poly-mer formed and the kinetics of the polymerization indicate a simple growth reaction at relatively low concentrations of initiator.   The struc-ture of polymers prepared with sodium and potassium alkoxides, on the other hand, is nearly statistical, which means that a complexing nature of the propagating end, if it exists at all, is not responsible for the growth. The effect of conversion results in an increase of the isotactic portion.

The effects of temperature and of benzene are similar.   Sodium alkoxide changes very much the stereoregularity in an isotactic direction.   There-fore the complexing character of the propagating chain may be assumed to increase.   Polymerizations initiated with potassium alkoxide are not affected very much either by dilution of the monomer or by temperature. Owing to the strong complexing character, no change could be expected in the case of polymerizations initiated by lithium alkoxide.   The effect of tetrahydrofuran results in an increased syndiotactic portion.   In this case no influence of the monomer concentration could be observed under the conditions studied.

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