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THE SEQUENCE LENGTH IN POLYMETHYL METHACRYLATE

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Abstract—The sequence length and tacticity of methyl methacrylate polymers prepared at 303–363°K in the presence of trichlorobromomethane as a transfer agent were measured from NMR spectra. The lengths did not change appreciably but there was an increase in syndiotacticity with increasing concentration of transfer agent. There is no marked change in tacticity with molecular weight.

INTRODUCTION

North and Richardson [1] have determined the mean sequence length distribution and the entropy of stereoregularity of finite molecular weight polymers by allowing for end-group concentration. They determined that the number fraction of sequences and the entropy of stereoregularity are molecular weight dependent for values below 10^5.

Low molecular weight polymers are more appropriate for NMR study of configuration because of their lower viscosities and potentially higher solubilities. Trichlorobromomethane transferred polymers were chosen for a study of end-group effects on the entropy of stereoregularity of free radical polymerization. Bovey and Tiers [2] have made a comprehensive study of the NMR spectrum of polymethyl methacrylate, and their method of deconvoluting the spectra was adopted.

EXPERIMENTAL

Purified methyl methacrylate (B.D.H. Ltd.) was polymerized *in vacuo* to about 5% conversion with benzoyl peroxide as initiator at various temperatures from 303 to 363°K. The reaction was followed dilatometrically. Molecular weights were controlled by varying initiator concentration, and by using a transfer agent (trichlorobromomethane) according to the Mayo equation,

$$\frac{1}{x_n} = C_i + C_s\frac{[S]}{[M]} \tag{1}$$

where $\bar{x}_n$ is the degree of polymerization, C_i and C_s the initiator and transfer agent constant, and [S] and [M] the transfer agent and monomer concentration.

The data listed by Barson *et al.* [3] for C_s were used to calculate $\bar{x}_n$ observed:

Temp./°K	303	318	333	348	363
$C_s \times 10^2$	4.3	5.5	5.8	9.3	10.7

Polymers were isolated by precipitation with excess methanol and purified by repeated precipitation from chloroform solutions with excess methanol. They were dried *in vacuo* at 323°K.

Isotactic polymer was prepared at 273°K using phenyl magnesium bromide as initiator. Low molecular weight material was removed by partial precipitation from benzene solution.

Molecular weight characteristics were determined by GPC on tetrahydrofuran solutions at 300°K. Four columns of divinyl benzene cross-linked polystyrene gels with permeabilities of 3×10^4, 1×10^4, 1×10^4 and $2\text{–}5 \times 10^3$ Å were used. A linear calibration of molecular weight and retention volume was obtained over the range $1\text{–}500 \times 10^3$. The q factor correlating peak count and molecular weight was taken as 39.70. Polymer characteristics are listed in Table 1.

Proton NMR spectra were measured on a Varian Associates Ltd. XL-100, 100 M-cycle spectrometer in deuterochloroform solutions with an external standard (TMS). The spectra were deconvoluted as outlined by Bovey and Tiers [2] and analysed from the areas under the curves, see Fig. 1. The method was found to be consistent (±1% for *m*,*r* lines) for repeated spectra on the same polymer sample but dependent on deconvolution procedure (±3% for *i*,*h* lines), see Table 2.

Assignment of the resonances listed by Bovey and Tiers was used in the analysis—

(a) 2 methyl protons—triads

Tacticity	triad	designation	assignment
syndio	d*l*d *l*d*l*	*s*	9.13τ

Table 1. Polymer characteristics

Serial no.	Temp./ °K	S/M	Molecular $\bar{M}_n \times 10^{-3}$*	Weight $\bar{M}_w \times 10^{-3}$*	D*
1	303	0.047	24.54	51.44	2.10
2	303	0.100	21.47	41.91	1.95
3	303	0.160	23.54	32.21	1.36
4	318	0.090	25.67	35.82	1.39
5	318	0.330	13.87	19.78	1.42
6	333	0.050	19.50	39.83	2.10
7	333	0.090	17.18	26.00	1.51
8	333	0.160	24.37	33.02	1.35
9	348	0.050	23.00	25.71	1.42
10	363	0.050	16.30	24.70	1.51
11	363	0.110	10.40	15.60	1.48
12	363	0.160	11.30	16.00	1.48

* G.P.C. $D = \bar{M}_w/\bar{M}_n$.

Table 2. Reproducibility of the analysis

Serial no.	*r*	*m*	*i*	*h*	*s*
1	0.89^4	0.10^6	0.02^1	0.27^7	0.69^3
	0.89^8	0.10^2	0.02^8	0.33^7	0.63^6
	0.89^6	0.10^4	0.03^0	0.29^5	0.67^5
	0.89^0	0.11^0	0.02^0	0.30^7	0.67^3
3	0.88^1	0.11^8	0.03^7	0.27^0	0.69^3
	0.88^3	0.11^7	0.01^5	0.27^4	0.71^1
	0.88^1	0.11^9	0.02^4	0.28^5	0.69^1

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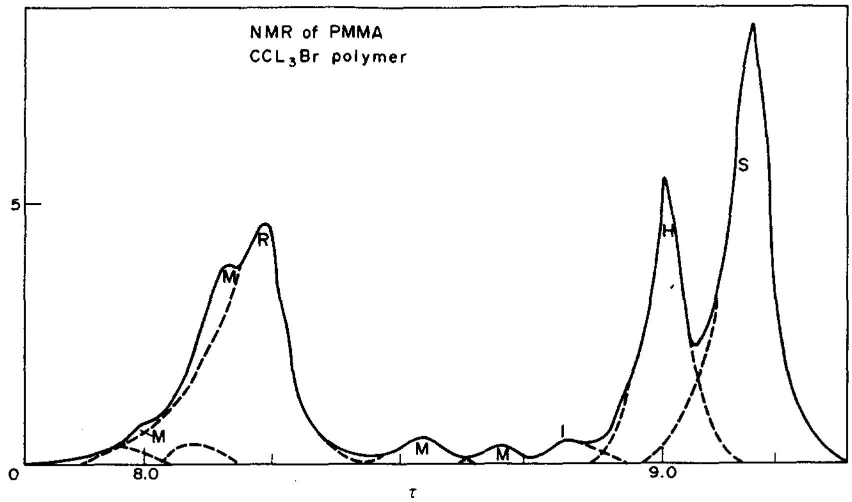

Fig. 1. Proton NMR spectrum of PMMA.

hetero	*ll*d dd*l*	*h*	8.98τ
iso	ddd *lll*	*i*	8.78τ
(b) Methylene protons—dyads			
racemic	d*l* *l*d	*r*	8.16τ
meso	*ll* dd	*m*	8.16τ*

*Quartet centred at 8.16τ.

In deconvoluting, the high field pair of the quartet centred at 8.16τ could be separated clearly from the racemic dyad at 8.16τ.

ANALYSES OF THE POLYMERS

Bovey and Tiers [2] further considered that the block sequences of isotactic and syndiotactic sequences can be derived as follows: for the chain,

$$\underbrace{ld\ldots ld\ ld\ ld\ ld}_{n_i}\ \underbrace{dddd\ldots ddd\ ld\ ld\ ld\ldots dl}_{n_s}\ ddd$$

The isotactic sequence is $(n_i + 1)$ units long with $(n_i - 1)$ ddd triads; the syndiotactic sequence is n_s units long with $(n_s - 1)$ d*l*d and *l*d*l* triads. If $x(n_i)$ is the number of isotactic sequences of length n_i, then there are

$$\sum_{n_i=1}^{\infty} x(n_i)(n_i - 1) \text{ ddd and } lll \text{ triads}$$

and

$$\sum_{n_s=1}^{\infty} x(n_s)(n_s - 1) \text{ d}l\text{d and } l\text{d}l \text{ triads.}$$

As isotactic and syndiotactic sequences must alternate, and neglecting end-group effects,

$$\sum_{n_i=1}^{\infty} x(n_i) = \sum_{n_s=1}^{\infty} x(n_s)$$

and

$$i/s = \sum_{n_i=1}^{\infty} x(n_i)(n_i - 1) / \sum_{n_s=1}^{\infty} x(n_s)(n_s - 1).$$

If the number average sequence lengths $\bar{n}_i$ and $\bar{n}_s$ are defined as

$$\bar{n} = \sum_{n=1}^{\infty} n\,x(n) / \sum_{n=1}^{\infty} x(n)$$

then

$$i/s = (\bar{n}_i - 1)/(\bar{n}_s - 1). \tag{2}$$

The total number of mesomeric dyads (dd and *ll*) is

$$\sum_{n_i=1}^{\infty} x(n_i)n_i$$

Table 3. Structure of transfer polymer (fractional composition)

Serial no.	*r*	*m*	*i*	*h*	*s*	$\bar{n}_i$	$\bar{n}_s$	*h*
1	0.89^6	0.10^4	0.02^4	0.31^0	0.66^6	1.4	12	0.15
2	0.88^6	0.11^4	0.01^9	0.28^2	0.70^0	1.2	9.6	0.18
3	0.88^1	0.11^9	0.02^4	0.27^6	0.70^0	1.3	9.6	0.18
4	0.86^1	0.13^3	0.04^5	0.30^4	0.65^1	1.7	11	0.16
5	0.81^8	0.18^2	0.03^6	0.32^0	0.64^3	1.3	5.7	0.30
6	0.86^6	0.13^4	0.02^7	0.31^3	0.66^0	1.3	8.4	0.21
7	0.84^9	0.15^1	0.03^2	0.35^8	0.61^0	1.3	7.6	0.22
8	0.83^2	0.16^8	0.03^6	0.32^6	0.63^8	1.3	6.5	0.26
9	0.86^8	0.13^2	0.04^2	0.39^0	0.56^8	1.8	12	0.15
10	0.85^0	0.15^0	0.03^8	0.40^3	0.56^0	1.5	8.6	0.20
11	0.83^8	0.16^2	0.03^4	0.36^4	0.60^2	1.3	6.9	0.24
12	0.82^2	0.17^8	0.04^4	0.35^2	0.60^4	1.4	6.5	0.25
Isotactic	0.972	0.028	0.852	0.055	0.093	11.2	0.3	0.20
Atactic	0.22	0.78	0.07	0.38	0.55	1.6	5.6	0.3

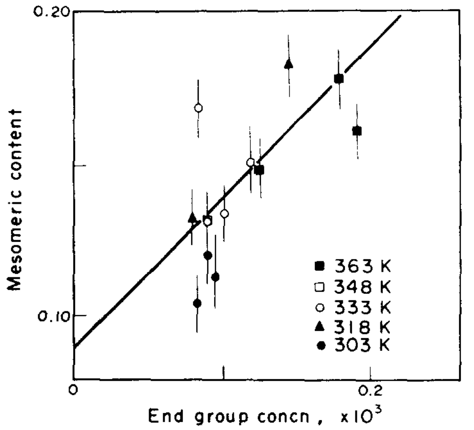

Fig. 2. Dependence of mesomeric content on end-group concentration.

and of racemic dyads (d*l* and *l*d)

$$\sum_{n_s=1}^{\infty} x(n_s)n_s$$

so that

$$m/r = \bar{n}_i/\bar{n}_s \tag{2a}$$

Combining (2) and (2a),

$$\bar{n}_i = (1 - i/s)/(1 - ir/ms) \tag{3}$$

$$\bar{n}_s = (1 - i/s)/[(m) - (i/s)] \tag{4}$$

Since heterotactic units occur between isotactic and syndiotactic blocks, their number is the number of blocks,

$$\sum_{n_i=1}^{\infty} x(n_i) + \sum_{n_s=1}^{\infty} x(n_s) = 2 \sum_{n_i=1}^{\infty} x(n_i)$$

for which

$$\bar{h} = 2/(\bar{n}_i + \bar{n}_s)$$

$\bar{h}$ is differentiated from h measured experimentally.

RESULTS

The proton NMR spectra of the polymers were analysed according to the above procedure, and the number-average sequence lengths are listed in Table 3 for the transfer polymer. For comparison, the analyses of free radical (designated atactic by Ref. [2]) and anionic (isotactic) polymers are included. In general, all the transferred polymer conformed to the structure of the atactic polymer. They all exhibited a low isotactic sequence length of about one unit, and a longer syndiotactic length, but consistent with free radical prepared polymers. The high heterotactic concentration also indicated short blocks.

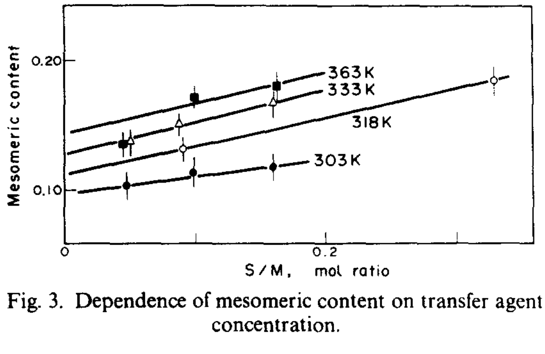

Fig. 3. Dependence of mesomeric content on transfer agent concentration.

Table 4. Arrhenius parameters (r/m ratio)

Ratio S/M	Entropy $\Delta(-\Delta S^{\ddagger})$ J mol K^{-1}	Enthalpy $\Delta(\Delta H^{\ddagger})$ kJ mol^{-1}	Degree of fit	Ref.
0	0.0 ± 0.4	3.2 ± 0.3		[5]
	4.0 ± 0.4	4.2 ± 0.4		[6, 7]
0.05	3.23 ± 3.40	6.31 ± 1.10	0.92	
0.10	3.09 ± 3.20	5.97 ± 1.33	0.91	
0.16	6.32 ± 5.55	6.76 ± 1.82	0.87	

When the mesomeric content of the polymers was plotted against end-group concentration, some dependence was observed, see Fig. 2, but there was no clear dependence on temperature of polymerization. However, if the reciprocal degree of polymerization calculated by Eqn. (1) was used instead of the end-group concentration, then a linear dependence was observed on mesomeric content, see Fig. 3. The ratio S/M in Eqn. (1) involved an almost constant value for [M] and so the dependence was considered to involve transfer agent concentration rather than polymer end-groups.

DISCUSSION

The dependence of the stereoregularity on molecular weight arises from an entropy term involving end-groups alone, and for the present polymers which are 55–70% syndiotactic there is little dependence of the entropy on molecular weight. Excluding samples 1–3, North and Richardson [1] calculations indicate that the entropy of stereoregularity for the remaining polymers lies within the narrow range 5.4–5.5 J mol^{-1} K^{-1}. There is a clear dependence of the tacticity on transfer agent concentration, see Fig. 3. Burleigh *et al.* [4] have observed a similar effect with polyvinyl chloride and polyacrylonitrile prepared in the presence of aliphatic aldehydes and considered it to be due to the presence of a complex between the aldehyde and monomer, or polymer chain. The effect of the complex might be to increase the steric hindrance on addition of monomer and so favour syndiotactic addition; such an effect would increase the difference between activation energies for syndiotactic and isotactic additions.

Assuming the same mechanism was involved with trichlorobromomethane, the NMR spectrum of monomer was measured in the presence of increasing amounts of trichlorobromomethane, but no chemical shifts were observed. Strong complexing with monomer must be ruled out.

It has been shown [5] that the mesomeric and racemic dyads in a polymer are determined by their rate constants of propagation, i.e.

$$r = k_r/(k_m + k_r)\,\text{etc.}$$

and so

$$r/m = [\exp\{\Delta S_r^{\ddagger} - \Delta S_m^{\ddagger}\}/R\cdot]$$

$$\times\ [\exp - (\Delta H_r^{\ddagger} - \Delta H_m^{\ddagger})/RT].$$

Plots of $\ln(r/m)$ against $1/T$ at various S/M ratios were linear, as indicated by their degree of fit ($\bar{y}^2$) with enthalpy differences between the two placements, which exhibited a tendency to increase with S/M ratio. They were greater than the values listed in the literature [5–7] for free radical polymerized polymethyl methacrylate. No significant differences were apparent in the differences in entropy of activation, which were in the range of values listed in the literature. There are large errors in both $\Delta(\Delta S\ddagger)$ and $\Delta(\Delta H\ddagger)$, however, which make these conclusions speculative.

CONCLUSIONS

It appears that the effects of end-groups on the entropy of stereoregularity in PMMA prepared by free radical initiators are not generally large over the range D.P. 50–500. Any dependence of the tacticity on molecular weight is masked by the effect of the transfer agent in favouring mesomeric addition in the propagation step. This effect is not due to complexing with either the monomer, polymer or propagating radical, since this would favour racemic addition, but the effect may be due to solvent effects on the transition state.

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