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Abstract

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THE INFLUENCE OF STRONG ELECTROSTATIC FIELDS DURING THE POLYMERIZATION OF METHYL METHACRYLATE ON THE STRUCTURE OF THE POLYMER FORMED

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As is known, a polymer with a predominance of a definite type of structure (syndiotactic, isotactic, stereoblock) can be obtained by using, under certain conditions, various ionic catalysts ([1], [2]). However, the formation of a polymer with a predominance of syndiotactic structure is also possible in free-radical homogeneous polymerization; this is due to different activation energies for chain growth of the syndiotactic and isotactic structures ([3]). For example, in the radical polymerization of methyl methacrylate (MMA), as the polymerization temperature is lowered, the fraction of syndiotactic structure increases to such an extent that polymethyl methacrylate (PMMA) obtained below 0°C is capable of crystallizing ([3]).

The ratio of the rate constants of chain growth in the formation of syndiotactic or isotactic structures may be written as:

$$\frac{K_s}{K_i} = \exp\left\{\frac{-\Delta F_s^{\ddagger} + \Delta F_i^{\ddagger}}{RT}\right\},$$

where K_s and $\Delta F_s^{\ddagger}$ are, respectively, the chain-growth rate constant and the free energy of activation in the formation of a polymer of syndiotactic structure; K_i and $\Delta F_i^{\ddagger}$ are, respectively, the chain-growth rate constant and the free energy of activation in the formation of a polymer of isotactic structure.

Bovey believes that, in the polymerization of MMA, the difference in the free energies of activation for chain growth of the syndiotactic and isotactic structures is determined only by the difference in the activation energies for the growth of these structures, which is equal to $\Delta(\Delta H_p^{\ddagger}) = 775 \pm 75$ cal/mole, while the difference in the activation entropies is equal to zero ([4]).

Apparently, the assumption $\Delta(\Delta S_p^\ddagger) = 0$ is not entirely accurate, and in a number of cases the contribution of the activation entropy to the free energy of activation is quite significant.

In the case of polymerization in an anisotropic medium—for example, in the solid state, in liquid crystals, in canal complexes, or in strong electrostatic fields—one may expect that it is precisely the entropy of activation of chain growth that will determine to a greater extent the structure of the polymer formed.

We investigated the polymerization of MMA in strong electrostatic fields (10^4—10^5 V/cm). The polymerization of MMA was carried out in special reactors with electrodes to which a high voltage was applied. Benzoyl peroxide, in an amount of 1 mole % relative to the monomer, was used as the initiator.

To determine the structure of PMMA formed during polymerization in an electrostatic field, we used the values I, calculated from infrared spectra, and the glass-transition temperatures T_g, obtained ob-

PMMA samples. The value I was determined from the following relations (^{5}):

$$I = \frac{I_1 + I_2}{2}; \qquad I_1 = 179\frac{A_{9.3}}{A_{10.1}} + 27; \qquad I_2 = 81.4\frac{A_{6.75}}{A_{7.2}} - 43.$$

The glass-transition temperatures T_g and the values of I for PMMA samples of different structure are given in Table 1 (^{5}).

Table 1

Structure		I
Syndiotactic	115	100—115
Stereoblock	60—95	40—80
Isotactic	45	25—35
Atactic	104	95—100

The conditions of the polymerization experiments, the values of I, and the glass-transition temperatures T_g of PMMA samples obtained at different electrostatic-field strengths are given in Table 2.

Comparison of the data in Tables 1 and 2 makes it possible to conclude that, during the polymerization of MMA in a strong electrostatic field, a polymer is formed with an increased content of syndiotactic structure. The effect of the electrostatic field on the structure of PMMA formed in toluene solution is considerably smaller than in bulk polymerization.

Table 2

Polymerization temp. t, °C	Field strength E, V/cm	Glass-transition temp. T_g, °C	Value I
Polymerization in bulk	**Polymerization in bulk**	**Polymerization in bulk**	**Polymerization in bulk**
50	0	106	101
50	0	106	97
50	$2.0 \cdot 10^4$	110	107
50	$2.5 \cdot 10^4$	111	106
50	$4.0 \cdot 10^4$	113	112
Polymerization in toluene solution	**Polymerization in toluene solution**	**Polymerization in toluene solution**	**Polymerization in toluene solution**
50	0.0	108	103
50	0.0	107	103
50	$6.0 \cdot 10^4$	112	106
50	$6.0 \cdot 10^4$	112	107
40	$7.0 \cdot 10^4$	113	109

However, up to the present time it has not been possible to determine quantitatively the increase in the fraction of syndiotactic structure in the polymer formed during polymerization in an electrostatic field. The NMR spectral data used for these purposes do not make it possible to determine the content of the various structures because of the high molecular weight of the polymer obtained under these conditions ([6,4]).

The introduction of a chain-transfer agent or the use of high initiator concentrations lowers the breakdown voltage of the reaction mixture to 10,000–15,000 V/cm, when the effect of the electrostatic field on the structure of the polymer formed is very slight.

The electrostatic field affects not only the structure of the polymer formed. The kinetics of MMA polymerization and the molecular weight also change during polymerization in a strong electrostatic field.

The future use of stronger electrostatic fields in MMA polymerization will make it possible to obtain PMMA samples with a substantial predominance of syndiotactic structure.

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Note: Figure translations are in progress. See original paper for figures.