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Functional Monomers and Polymers. XLV.* Activation Parameters for Polymerization of N-β-Methacryloyloxyethyl Type Monomers Containing Nucleic Acid Bases

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ABSTRACT

In order to determine the effect of functional structure of ester groups on the stereoregularity of polymers, polymerization of N-β-methacryloyloxyethyl type monomers containing nucleic acid bases was made by using a free-radical initiator. From the NMR spectrometric determination of the stereoregularity of the polymers obtained, it was found that for polymerization of the monomer with adenine as the side group in dimethyl sulfoxide solution, syndiotactic placement appears to be favored by the additional enthalpy of activation required for isotactic placement.

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*For part XLIV in this series: see M. Sato, K. Kondo, and K. Takemoto, in press.

INTRODUCTION

In a previous paper, copolymerization of the N-β-methacryloyloxyethyl derivative of adenine (MAOA) with that of thymine (MAOT) or uracil (MAOU) has been reported, and it has been shown that interaction between complementary nucleic acid bases plays a role in the propagation step of the copolymerization [1, 2]. In connection with this work, the stereoregularity of a series of polymers of MAOA, MAOT, MAOU, and N-β-methacryloxloxyethyltheophylline (MAOThe) prepared by a free-radical polymerization from their corresponding monomers in various solvents has been determined [3]. The stereoregularity of poly(methyl methacrylate) (poly-MMA) has been studied in detail by Bovey [4], Fox and Schnecko [5], and Otsu et al. [6], and from their data, values of about 1 kcal for $\Delta\Delta H^\ddagger$ and about 1 e. u. for $\Delta\Delta S^\ddagger$ were obtained. A bulky side chain, such as a menthyl group, appears to encourage isotactic placement, and in the case of poly(menthyl methacrylate), the value of $\Delta\Delta H^\ddagger$ is about 0.5 kcal, that is, only about half of the value for MMA [7].

This paper concerns the determination of the values of the activation parameters in the polymerization of N-β-methacryloyloxyethyl type monomers having nucleic acid bases as the side groups, and a discussion of how the specific base-base interaction reflects on the stereoregularity of the polymers in question.

EXPERIMENTAL

All the monomers, that is MAOA, MAOT, MAOU, and MAOThe, were prepared according to the method reported earlier [8]. Purification of all the reagents was achieved in the usual manner, and the polymerization procedure in sealed tubes, as well as the rate determination technique by gravimetry were carried out as reported in preceding papers [9, 10]. At the temperatures below 40°C, polymerization was carried out by irradiating with a 100 W high-pressure mercury vapor lamp (Toshiba SH-100 UV-2, 300-600 nm) at a distance of 10 cm.

The stereoregularity of the polymers obtained was determined by NMR spectrometry as reported in a previous paper [3].

RESULTS AND DISCUSSION

Polymerization of the four types of monomers chosen was performed in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dioxane, and ethanol solutions in the temperature range between 20

TABLE 1. Stereoregularity of Poly-MAOA

Polymerization[a]			Stereoregularity (%)			
Solvent	Temp. (°C)	$R_p \times 10^4$, (mole/liter-sec)	I	H	S	σ
DMSO	20	1.7	4	31	65	0.19
	40	2.0	6	36	58	0.24
	60	1.7	8	39	53	0.27
	80	0.98	10	40	50	0.29
	90	0.72	11	42	47	0.31
DMF	20	0.25	6	38	56	0.25
	40	0.62	7	40	53	0.27
	60	0.63	8	40	52	0.28
	75	0.46	9	41	50	0.29

[a] Conditions for polymerization; [monomer] = 4.0×10^{-2} mole/liter, [AIBN] = 2.0×10^{-3} mole/liter.

and 90°C, azobisisobutyronitrile (AIBN) being used as an initiator. The rate of polymerization and the tacticities of the polymers obtained are shown in Table 1 as an example. As can be seen, the polymers seem not to differ considerably in stereoregularity at 60°C in various solvents. The only exceptional result obtained was the polymerization of MAOA at lower temperature, in which syndiotacticity of the polymers was found to increase in DMSO solution.

The Bovey single-σ plots [4] for poly-MAOA obtained in DMSO solution are shown in Fig. 1, where σ is defined as the probability that an adding monomer generates the same configuration as that of the end of a growing chain. It was found from the figure that the observed values are consistent with the theoretical curves. Therefore, it can be assumed that this polymerization obeys Bernoullian statistics.

The activation enthalpy and entropy differences between isotactic and syndiotactic additions are given by Eqs. (1)-(3) [11]:

$$k_i/k_s = \exp\{(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})/R\}\exp\{-(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})/RT\} \qquad (1)$$

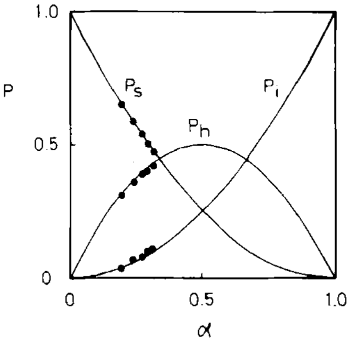

FIG. 1. Probabilities P_i, P_s, and P_h of formation of isotactic, syndiotactic, and heterotactic triads as a function of Bovey-Tiers σ values for poly-MAOA prepared in DMSO solution.

$$\Delta\Delta S^{\ddagger} = \Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$$

$$\Delta\Delta H^{\ddagger} = \Delta H_i^{\ddagger} - \Delta H_s^{\ddagger} \qquad (2)$$

where

$$k_i/k_s = P_I/P_S$$

$$P_I = P_i + (P_h/2)$$

$$P_S = P_s + (P_h/2) \qquad (3)$$

By applying the experimental results to Eqs. (1), (2), and (3), Figs. 2 to 5 are plotted. From these figures, values summarized in Table 2 were obtained.

As can be seen from Table 2, values of both activation parameters differ in DMF and in DMSO solution, and thus the stereoregularity of poly-MAOA was affected by the type of solvent. However, these values seem not to differ markedly from each other for the case of the polymerization of MAOT. For the polymerization of MAOU, these values were small and similar to each other in DMF, dioxane, and ethanol.

It is a generally accepted view that for the free-radical polymerization, syndiotacticity of the polymers tends to decrease with a decrease in the steric factor of the side groups. On comparing our present results with those given by Matsuzaki [12], the steric factors of N-β-methacryloyloxyethyl type of monomers having nucleic acid

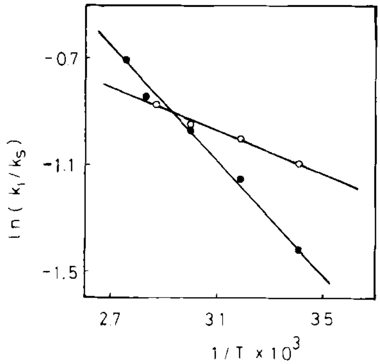

FIG. 2. Arrhenius plot of the tacticity of poly-MAOA: (●) in DMSO; (○) in DMF.

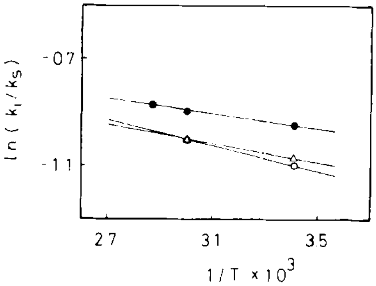

FIG. 3. Arrhenius plot of the tacticity of poly-MAOU: (●) in ethanol; (△) in dioxane; (○) in DMF.

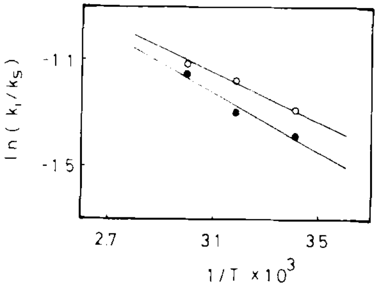

FIG. 4. Arrhenius plot of the tacticity of poly-MAOT: (●) in DMSO; (○) in DMF.

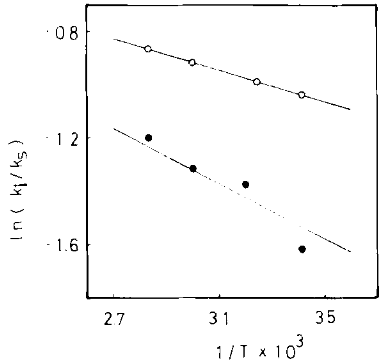

FIG. 5. Arrhenius plot of the tacticity of poly-MAOThe and poly-MMA: (○) MAOThe in DMSO; (●) MMA in DMSO.

TABLE 2. Activation Parameters

Monomer	Solvent	$\Delta\Delta H^\ddagger$ (cal/mole)	$\Delta\Delta S^\ddagger$ (e. u.)
MAOA	DMSO	2100	4.4
	DMF	790	0.57
MAOU	DMF	490	-0.26
	Dioxane	360	-0.46
	Ethanol	300	-1.5
MAOT	DMSO	1100	0.51
	DMF	870	0.28
MAOThe	DMSO	620	0.06
MMA	DMSO	900	0.12

bases should be regarded as similar to that of 2-phenethyl methacrylate. However, the value of $\Delta\Delta H^\ddagger$ for MAOA obtained here was quite large compared with those for MAOT, MAOU, and MAOThe, and this could not be explained only by considering the steric factor in this case.

As the monomers concerned in the present work contain nucleic acid bases as the side groups, interaction between a base in a monomer and that in a unit at a growing chain end of the polymers may play an important role. If the hydrogen-bonding interaction between nucleic acid bases is important, syndiotactic addition would be more favorable because of stereochemical factors [3]. We have already reported the result that the intramolecular interaction between adenine bases is stronger than that between any other pyrimidine bases, and this seems to be reflected in the peculiar feature of the polymerization of MAOA in DMSO solution; in all other cases of polymerization, the values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ obtained are rather common and not peculiar (as in the case of MAOA); probably because of solubility factors, no such specific feature is apparent. This is also supported by the fact that amino protons of adenine ring of the polymer show a downfield shift which could not be observed in the case of pyrimidine derivatives [3]. For the polymerization of MAOThe in DMSO solution, the values of activation parameters obtained were also common ones, as expected, because theophylline is not a nucleic acid base and has no self-association ability.

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