Stereocontrol in Free Radical and Ionic Polymerizations. II. Activation Energies of Stereocontrol of Ionic Polymerizations

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LETTER TO THE EDITOR

Stereocontrol in Free Radical and Ionic Polymerizations. II. Activation Energies of Stereocontrol of Ionic Polymerizations

In a previous paper [1], a compensation effect was shown to exist between the difference of activation enthalpies $(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})$ for the formation of iso- and syndiotactic dyads, respectively, in free radical propagated polymerizations and the corresponding difference of activation entropies $(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})$. It is thus of interest whether or not a similar compensation effect is exhibited by ionic polymerizations.

Indeed, published measurements [2] on cationic polymerizations of vinyloxytrimethylsilane show the existence of a compensation effect after plotting $(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})$ against $(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})$ (Fig. 1). The polymerizations have been carried out with EtAlCl$_2$ in toluene, SnCl$_4$ in CH$_2$Cl$_2$, and SnCl$_4$ in NO$_2$Et (Table 1). The relationship between activation enthalpies and entropies can be expressed by

$$(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}) = (\Delta \Delta H^{\ddagger})_0 + T_0 (\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}) \text{ cal/mole} \qquad (1)$$

$$(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}) = (150 \pm 22) + (280 \pm 40)(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}) \text{ cal/mole}$$

$T_0 = 280°K$ is the temperature at which polymerizations in different solvents lead to equal tacticities. This temperature has been referred to as the "tactically isostatic temperature" [4].

The existence of a compensation effect in cationic polymerizations is surprising with respect to the known complicated equilibria between free ions, solvent separated ion pairs, intimate ion pairs, and ion associates (see the papers of the Szwarc and Schulz schools on anionic polymerizations, e.g., Ref. 5).
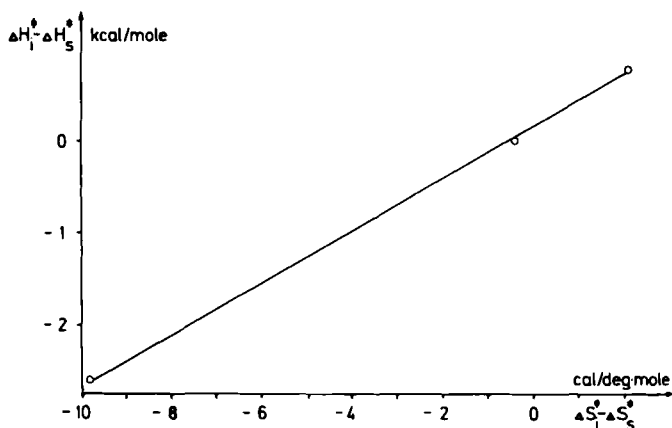
Fig. 1. Compensation effect between the differences $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ of activation enthalpies for the formation of isotactic and syndiotactic dyads and the corresponding differences of activation entropies $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ for the cationic polymerization of vinyloxytrimethylsilane (data of Murahashi [2]).

Table 1. Difference in Activation Enthalpies and Activation Entropies for the Formation of Isotactic and Syndiotactic Dyads in the Cationic Polymerization of Vinyloxytrimethylsilane and Dielectricity Constants ϵ_0 of the Solvents Used in Polymerization

Initiator/solvent	$\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ (cal/mole) [2]	$\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ (cal mole^{-1} deg^{-1}) [2]	ϵ_0 [3]
$SnCl_4/NO_2 Et$	780	2.1	28.06 (30°C)
$SnCl_4/CH_2 Cl_2$	0	–0.4	9.08 (20°C)
$Et AlCl_2/toluene$	–2600	–9.8	2.38 (25°C)

Because an increasing polarity of the solvent will shift these equilibria in favor of the free ions, one can try to extrapolate $(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})$ and/or $(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})$ toward infinite polarity to obtain the values corresponding to free ions. As a measure of polarity, dielectricity constants are normally used. A plot of both $(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})$ and $(\Delta H_i^{\ddagger} - \Delta S_s^{\ddagger})$ vs $1/\epsilon_0$ shows a linear dependence between these quantities, too, (Fig. 2) which can be expressed by
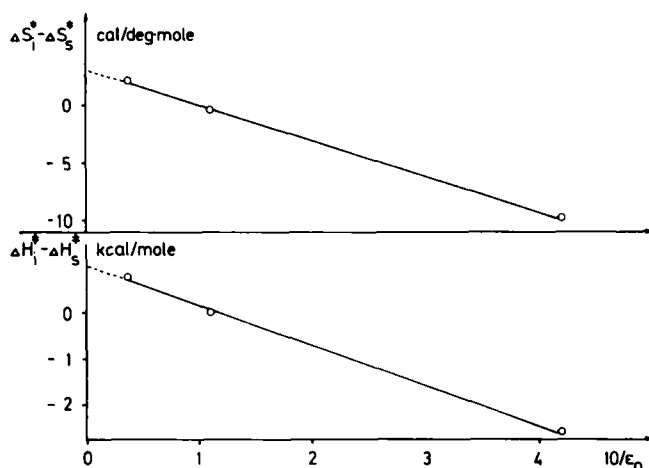
Fig. 2. Dependence of $\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$ and $\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$ on the reciprocal dielectricity constant of the solvent (data of Murahashi [2]).

$$(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}) = (\Delta\Delta H^{\ddagger})_{\infty} + B_H(1/\epsilon_0)$$
$$= (1160) \pm 88) - (9300 \pm 520)(1/\epsilon_0) \tag{2}$$

$$(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}) = (\Delta\Delta S^{\ddagger})_{\infty} + B_S(1/\epsilon_0)$$
$$= (3.10 \pm 0.061) - (31 \pm 1.1)(1/\epsilon_0) \tag{3}$$

In this treatment, the (normally small) temperature dependence of the dielectricity constants ϵ_0 of the solvents as well as the change of ϵ_0 after addition of monomer has been neglected.

If the quantities $(\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})_{\infty} = (1160 \pm 88)$ cal/mole and $(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})_{\infty} = (3.10 \pm 0.061)$ cal/mole^{-1} deg^{-1} really reflect the behavior of free ions, these quantities can be expected to be independent of the concentration of the monomer in the monomer/solvent mixture. No experiments are known which can be used as a test of this consequence. Furthermore, it remains to be shown how the activation enthalpies and entropies of free carbonium ion polymerizations compare with the corresponding data of free radical and free carbeniate ion polymerization, especially with respect to the structure of the ions and radicals (planar, pyramidal). Other open questions concern the influence of the environment on tacticity (solvation, influence on transition state) and naturally in ionic polymerizations

the respective influences of all propagating species on stereocontrol. The determination of the dependence of activation enthalpies and activation entropies on dielectricity constants of the solvent (or better of solvent/ monomer mixture at low conversions) may be a very useful technique for the exploration of the stereocontrol of ionic polymerizations in this respect.

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