(4) G. F. Endres and J. Kwiatek, *J. Polym. Sci.*, **58**, 593 (1962).
(5) D. M. White, *J. Org. Chem.*, **34**, 297 (1969).
(6) A variety of catalyst systems can be used to prepare the low oligomers; see, e.g., ref 1, p 541, or G. C. Cooper and J. G. Bennett, U.S. Patent 3 661 848 (1972).
(7) Initiator **2** is formed as a byproduct in low yield during 2,6-dimethylphenol polymerization.[1]
(8) The use of narrow MWD PPO as a standard for GPC calibration will be described in a later report.
(9) Initiator **2** is slowly reduced to 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl[10] which co-redistributes with **1**.[5] To minimize co-redistribution yet provide initiation, **2** was added in portions.
(10) A. S. Hay, *Tetrahedron Lett.*, 4241 (1965).

Comments on the Kinetics of Cationic Polymerization of Tetrahydrofuran

STANISŁAW PENCZEK

Polish Academy of Sciences, Center of Molecular and Macromolecular Studies, 90-362 Łódź, Poland.

Received April 11, 1979

Recently, Professor Szwarc proposed a new interpretation of the kinetics of polymerization of THF, stemming from the new way of treating the immediate surroundings of the growing macrocations and/or macroion pairs.[1] According to this interpretation, propagation in solvents of low polarity proceeds in clusters constituted of THF (monomer) molecules and polymer segments in the proportion identical with that in the bulk solvent. Solvent molecules, according to this treatment, do not enter the immediate surroundings of the growing macrocations.

Starting from this view, the kinetics of propagation is treated as a process in which the real rate constants of propagation are the same for various THF/solvent mixtures.

This interesting new proposal refers to our work,[2,3] in which we showed that in the polymerization of THF in CCl_4 solvent the rate constant of propagation k_p, expressed as a second-order rate constant, increases with decreasing starting monomer concentration $[THF]_0$. On the other hand, propagation is internally first order on monomer in this solvent as well as in bulk. We interpreted the observed dependence of k_p on $[THF]_0$ in terms of the influence of polarity of the medium on k_p, tacitly assuming that CCl_4 molecules are present in the immediate surroundings of macrocations. By influence of polarity, we understand the change of the electrostatic energy of ions with dielectric constant as well as specific solvating action. We have at present no way to dissect these two effects.

According to Szwarc's proposal, the difference observed by us could come from the formal treatment of the kinetics, namely Szwarc proposes to use the "unimolecular rate constant" k_u, which, at least for the THF/CCl_4 system, does not depend on $[THF]_0$ and is equal to $k_p[THF]_0$, where k_p is the second-order rate constant of propagation determined in our studies and is found to be dependent on $[THF]_0$ for the CCl_4 solvent.

One has to agree that the dependence of k_p on $[THF]_0$ in CCl_4 solvent, taken as an isolated fact, could have been alternatively interpreted in this way.

The simplest proof for the treatment outlined above would be the constancy of k_u. Simple calculations, based on our data already published,[2] give, e.g., $k_u = 0.42\ s^{-1}$ ($[THF]_0 = 12.3\ mol\ L^{-1}$) and $k_u = 0.32\ s^{-1}$ ($[THF]_0 = 8.0\ mol\ L^{-1}$) in CCl_4 solvent. Thus, the difference in k_u is even larger than that between our k_p values (see below) for the same conditions. Thus, either an assumption, treating the ratio [THF]/[polymer segment] in proximity of the growing species, is too rough an approximation or, as we are still inclined to suppose, the solvent molecules are indeed present in the immediate proximity of the growing species.

Table I

solvent	$[THF]_0$, mol L^{-1}	10^2k_p, mol^{-1} L s^{-1}	$\Delta H^{\ddagger}_p$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}_p$, cal mol^{-1} deg^{-1}
THF	12.3	3.4	14.0	−17.5
CCl_4	8.0	4.0	9.0	−33.0
CCl_4	7.0	4.3	8.4	−36.0

[a] $\Delta H^{\ddagger}_p$ calculated for k_p are equal to $\Delta H^{\ddagger}_p$ calculated for k_p because $k_u = k_p[THF]_0$ (by definition).

Moreover, we observed for the THF/CCl_4 system the large change of the activation parameters $\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ (mostly compensating each other) in spite of only small changes of the corresponding k_p; this is illustrated in Table I. According to Szwarc, the CCl_4 molecules are absent in the immediate proximity of the growing species, and the solvation of macrocations by THF and poly(THF) segments proceeds with equal probability. Thus, one should not expect such a change of $\Delta H^{\ddagger}_p$ with the changing starting concentration of THF. Indeed, according to Szwarc's treatment, merely the proportion of THF and poly(THF) would change in the surroundings of the macrocations with changing $[THF]_0$.

We explained the change of $\Delta H^{\ddagger}_p$ and $\Delta S^{\ddagger}_p$ with the [THF]/[CCl_4] ratio[2,3] by assuming that in the immediate proximity of the active species all of the components of the mixture are present, namely THF, the poly(THF) segments, and CCl_4 molecules. Consequently, the higher the proportion of THF molecules around macroions in the ground state the higher the enthalpy of activation.

More recently, the polymerization of THF was studied in polar solvents, namely in CH_2Cl_2 and CH_3NO_2.[4] In CH_2Cl_2 solvent, the second-order k_p is almost independent of $[THF]_0$ at 25°C. In CH_3NO_2, which is much more polar and polarizable than THF, the dependence of k_p on $[THF]_0$ is opposite to that observed for CCl_4; namely with increasing $[THF]_0$, k_p also increases. Thus, for all of the three systems there is a monotonous trend, and with increasing polarity, expressed by the bulk dielectric constants, the k_p slightly decreases. There is no indication that the mechanism of propagation changes when passing to CCl_4 as the solvent.

As mentioned above, it is difficult at present to discuss separately the influence of the electrostatic energy of ions on the rate parameters influenced mostly by the dielectric constant at the proximity of ions and of solvation of ions, related to the solvating power of the components of the system. Apparently, for systems with lower dielectric constants, the influence of changes of the electrostatic energy may prevail.

There are a number of systems known in physical organic chemistry behaving very similarly to the cationic polymerization of THF discussed above, and they all belong to the group of reactions between ions and polar molecules. The ground states in these reactions have more ionic character than the corresponding transition state,[5] and the values of the activation parameters are usually directly related to the solvation–desolvation phenomena when passing from the ground state to the transition state.

Thus, the data available at present do not allow us to adopt for the polymerization of THF the idea of the monomer–polymer clusters around the growing species. However, this original approach, stressing the importance of the noncontinuity of ionic solutions in the ionic polymerizations, will certainly find its place in describing systems with stronger nonspecific interactions.

References and Notes

(1) M. Szwarc, *Macromolecules*, **11**, 1053 (1978).
(2) K. Matyjaszewski, P. Kubisa, and St. Penczek, *J. Polym. Sci.*, **13**, 763 (1975).
(3) St. Penczek and K. Matyjaszewski, *J. Polym. Sci., Polym. Symp.*, **56**, 255 (1976).
(4) K. Matyjaszewski, St. Slomkowski, and St. Penczek, *J. Polym. Sci.*, in press.
(5) J. F. Coetzee and C. D. Richie, Eds., "Solute-Solvent Interactions", Marcel Dekker, New York, 1969.

Diffusion and Surface Activity of Block Copolymers in Polystyrene Melts: Effects of Copolymer Molecular Weight and Morphology

GEORGE L. GAINES, Jr.

General Electric Research and Development Center, Schenectady, New York 12301. *Received June 7, 1979*

Several years ago, the time-dependent surface-tension changes in a polystyrene melt containing small amounts of surface-active styrene–dimethylsiloxane block copolymer were reported.[1] It was concluded that the early stages of adsorption were limited by diffusion of the block copolymer additive to the surface, and it was found that reasonable values of diffusion constants could be extracted from the data. During the course of that work, fragmentary results for some other copolymer additives were obtained but were not reported. In view of recent interest in diffusion in polymer melts and mixtures,[2,3] these results have been reexamined and are presented and discussed here.

Experimental Section

The styrene homopolymer used ($\bar{M}_n = 9290$) and all experimental procedures were the same as those previously described.[1] Two additional A-B block copolymers were used as additives: one had $\bar{M}_n$(osmotic) = 6800 and contained 14.6% Si (corresponding to styrene $(S)_{40}$–dimethylsiloxane $(D)_{36}$), while the other had $\bar{M}_n$ = 24 200 and contained 16.7% Si (S_{129}–D_{144}). In addition, a multiple sequence block polymer,[4] having the design structure $(D_{25}S_{50}D_{25})_x$, 16.0% Si, $\bar{M}_n$ = 69 400 (hence $\bar{x}$ = 7.8), was used. Since these samples were not subjected to the fractionation applied to the earlier-described block polymer (S_{75}–D_{77}), it may be assumed that they were more polydisperse.

Results and Discussion

The experimental results are presented in Figures 1 and 2. According to our earlier analysis,[1] during the early stages of adsorption, while diffusion through the bulk is limiting the arrival of surfactant at the interface, the surface tension lowering is expected to be proportional to $t^{1/2}$. In the case of the three earliest points for the system containing the copolymer S_{129}–D_{144}, this relationship is obeyed. Accordingly, the diffusion constant can be estimated from the slope of a plot of $(\gamma_0 - \gamma)$ vs. $t^{1/2}$ (cf. eq 3 of ref 1) as 5.7×10^{-9} cm^2/s, and this value has been used to construct the solid curve in Figure 1.

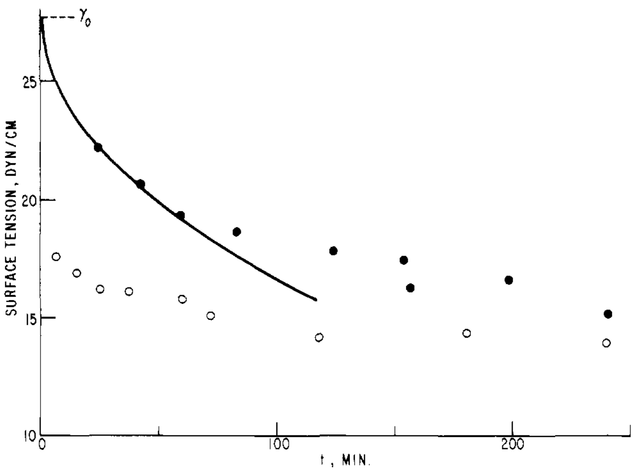

Figure 1. Surface tension at 200 °C as a function of time for blends of polystyrene with 0.1 wt % copolymer $S_{40}D_{36}$ (○) or $S_{129}D_{14}$ (●). The solid line is calculated for diffusion-controlled adsorption. γ_0 is the surface tension of polystyrene at 200 °C.

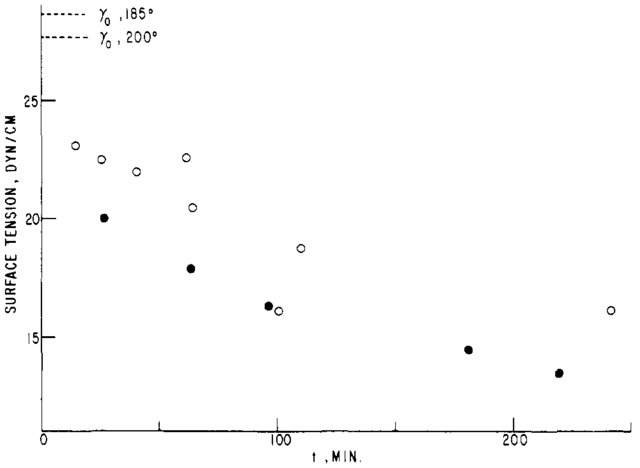

Figure 2. Surface tension of a blend of polystyrene plus 0.1 wt % copolymer $(D_{25}D_{50}D_{25})_{7.8}$ at 185 °C (○) and 200 °C (●). γ_0 is the surface tension of pure polystyrene at the indicated temperature.

Table I
Diffusion Constants for Block Copolymers in Polystyrene, Estimated from the Rate of Surface Tension Lowering

copolymer	T, °C	D, cm^2/s
$S_{40}D_{36}$	200	$>5.3 \times 10^{-9}$
$S_{75}D_{77}$	200	3.6×10^{-8} [a]
$S_{129}D_{144}$	200	5.7×10^{-9}
$(D_{25}S_{50}D_{25})_{7.8}$	185	$>9.2 \times 10^{-8}$
	200	$>8.3 \times 10^{-8}$

[a] From ref 1.

Most of the data presented here pertain to the long-time slow approach to adsorption equilibrium, for which no detailed interpretation is available. However, since diffusion to the surface must precede adsorption, it is possible to use the earliest measured surface pressure value to estimate a lower limit for the diffusion constant. Values obtained in this way are listed in Table I. It must be recognized, of course, that these are lower limit values; there is no way to estimate from the present results how much larger the correct values are, and in fact they may be very much larger.

It is interesting to note that the multiple sequence block copolymer appears to have a diffusion constant substantially larger than those for the AB types. Since we have no information on the polydispersity of these samples, it is possible that this result merely reflects the presence of a low molecular weight component. (It should also be noted that the use of a molar concentration in the estimation of the diffusion constant will lead to a different value of D if the molecular weight value is altered.) Nevertheless, it seems logical that the multiple sequence copolymer, with its styrene segments surrounded by si-

0024-9297/79/2212-1011$01.00/0