Influence of the polymerization temperature on the relative reactivities of acenaphtylene , α-methylstyrene and styrene

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The influence of temperature of polymerization on the values of reactivity ratios in the copolymerization of the systems acenaphthylene–styrene and acenaphthylene–α-methylstyrene has been studied. The values of activation enthalpy and entropy differences have been determined. It appears that for the systems α-methylstyrene–styrene and α-methylstyrene–acenaphthylene, the selection is enthalpically controlled and in the case of the system acenaphthylene–styrene is entropically controlled.

INTRODUCTION

Studies of the influence of experimental conditions on the reactivity of acenaphthylene have previously been published[1,2]; however, similar studies have not been carried out with the α-methylstyrene–acenaphthylene system. It is interesting to examine this system in order to see if the relatively low ceiling temperature of α-methylstyrene disturbs the determination of the reactivity ratios, as it appears to do for some other systems[3], and if the selectivity between the various monomers is enthalpically or entropically controlled.

EXPERIMENTAL

The monomers used were commercial products freshly distilled before copolymerization.

Copolymerizations were carried out under dry nitrogen. $TiCl_4$ was purified by distillation and methylene chloride was purified by the method of Nguyen Anh Hung[4]. Reactivity ratios were determined according to the procedures of Kelen and Tüdös[5].

RESULTS AND DISCUSSION

The variations of r_1 and r_2 for the system acenaphthylene (subscript 1)–α-methylstyrene (subscript 2) are reported in *Table 1* and *Figure 1*.

Table 1 Variations of r_1 and r_2 with the temperature of polymerization for the system acenaphthalene (subscript 1)–α-methylstyrene (subscript 2). [M] = 0.1 mol/l; [$TiCl_4$] = 0.001 mol/l; solvent CH_2Cl_2

t(°C)	T_k	$1/T$	r_1	r_2	r_1r_2	Log r_1	Log r_2
−70	203	0.0049	0.075	8.3	0.62	−2.59	2.12
−50	223	0.0045	0.17	3.64	0.62	−1.77	1.29
−30	243	0.0041	0.58	0.77	0.45	−0.54	−0.26
0	273	0.0037	0.92	0.20	0.18	−0.08	−1.61
20	293	0.0034	1.49	0.1	0.15	0.40	−2.30

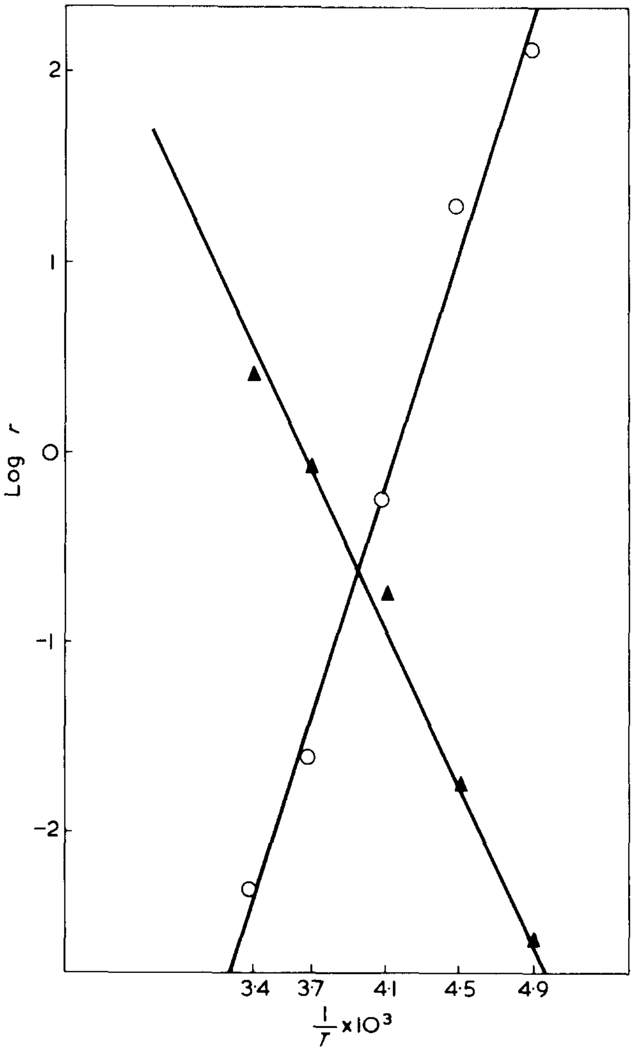

Figure 1 Copolymerization of the system acenaphthylene (subscript 1)–α-methylstyrene (subscript 2). Variations or log r_1 (○) and log r_2 (▲) with respect to $10^3/T$ (T = absolute temperature of copolymerization)

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Table 2 Values of enthalpy and entropy differences for styrene (S) acenaphthylene (A) and α-methylstyrene (αS)–acenaphthylene (A) systems

ΔH (cal/mol)		ΔS (cal/mol K)	
$\Delta H_{AA} - H_{AS}$	$= 1.01$	$\Delta S_{AA} - S_{AS}$	$= 9.74$
$\Delta H_{SS} - H_{SA}$	$= -0.36$	$\Delta S_{SS} - S_{SA}$	$= -5.14$
$\Delta H_{AA} - H_{A\alpha S}$	$= 4.06$	$\Delta S_{AA} - S_{A\alpha S}$	$= 14.88$
$\Delta H_{\alpha S\alpha S} - H_{\alpha SA}$	$= -6.25$	$\Delta S_{\alpha S\alpha S} - S_{\alpha SA}$	$= -26$

Table 3 Variations of the reactivity ratios relative to the styrene (S) –acenaphthylene (A) and α-methylstyrene (αS)–acenaphthylene (A) systems with respect to temperature

(S)–(A)	(αS)–(A)
$r_{AS} = 130 \exp(-505/T)$	$1/r_{AS} = 0.008 \exp(505/T)$
$r_{AS} = 0.006 \exp(180/T)$	$1/r_{SA} = 170 \exp(-180/T)$
$r_{A\alpha S} = 1701 \exp(-2030/T)$	$1/r_{A\alpha S} = 0.0006 \exp(2030/T)$
$r_{\alpha SA} = 2 \times 10^{-6} \exp(3100/T)$	$1/r_{\alpha SA} = 4.4 \times 10^{5} \exp(-3100/T)$

The variations with respect to temperature of $\log r_1$ and $\log r_2$ are given by the classical relations:

$$\log r_1 = (S_{11} - S_{12})\,[R - (\Delta H_{11} - \Delta H_{12})/RT]$$

$$\log r_2 = (S_{22} - S_{21})\,[R - (\Delta H_{11} - \Delta H_{12})/RT]$$

The subscripts S, αS and A represent styrene, α methylstyrene and acenaphthylene, respectively. In the following section, the first subscript represents the cation and the second represents the monomer. For instance, ΔH_{AS} is the activation enthalpy relative to the attacks of the polyacenaphthyl carbocation by the monomer styrene.

From *Figure 1* and from our previous results[2], the values of entropy and enthalpy differences for the systems acenaphthylene–α-methylstyrene and acenaphthylene–styrene can be obtained; these are reported in *Table 2*. From these values, the relations shown in *Table 3* have been obtained.

From *Table 3* the following classifications of the monomers with regard to their reactivity towards the polyacenaphthyl cation can be obtained, according to which term is considered:

Exponential term:
α-methylstyrene > styrene > acenaphthylene
Pre-exponential term:
acenaphthylene > styrene > α-methylstyrene
$1/r_1$ (experimental reactivity):
α-methylstyrene > acenaphthylene > styrene

Close examination of these classifications shows that the selection is entropically controlled for the acenaphthylene–styrene system and enthalpically controlled for the α-methylstyrene–styrene and α-methylstyrene–acenaphthylene systems. Calculation of the activation energies according to the method of Yonezawa[6] leads to the following classification:

α-methylstyrene ≫ acenaphthylene > styrene

This proves that in the case of α-methylstyrene the reactivity is so much increased by the inductive effect of the methyl group that the selection in the systems where this monomer is present, is enthalpically controlled. On the other hand, for the system acenaphthylene–styrene the reactivities due to electronic effects are very close and the selection is mainly controlled by solvation–desolvation phenomena which shows a dominance of the entropic term.

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