

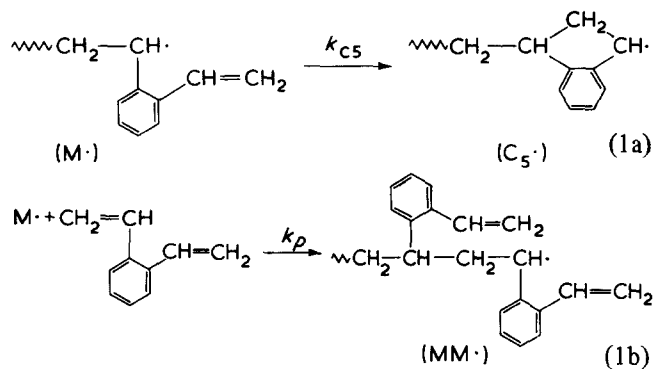
Free radical polymerization of unconjugated dienes: 18. Cyclopolymerization of *o*-divinylbenzene at 70°C

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The free radical polymerization at 70°C of *o*-divinylbenzene in toluene solutions takes place according to a cyclopolymerization mechanism. By fitting the experimental data with two different relationships between the mole fraction of residual unsaturation in the polymers and the monomer concentration at which they were obtained, it has been possible to show that, in the chain propagation steps, intramolecular cyclization could occur involving the two monomeric units entered last in the polymer chain, with formation of seven-membered ring structures.

Some years ago Aso *et al.*⁹ reported that *o*-divinylbenzene (*o*-DVB) undergoes free radical cyclopolymerization, and assumed that in the chain propagation steps the following reactions take place:



The cyclization ratio $r_c = k_{c5}/k_p$, evaluated by employing a kinetic relationship (derived on the basis of the above reactions) between the mole fraction of residual unsaturation in the polymers and the monomer concentration at which they were prepared, was found to vary from 3.60 mol/l to 1.89 mol/l when the polymerization temperature decreases from 90° to 20°C. By plotting the r_c values reported by Aso¹ as a function of $1/T$, according to the equation:

$$\ln r_c = \frac{\Delta S_c^\ddagger - \Delta S_p^\ddagger}{R} - \frac{E_c - E_p}{RT} \quad (2)$$

where E_c and E_p are the activation energies for reactions (1a) and (1b), respectively, and ΔS_c^\ddagger and ΔS_p^\ddagger are the corresponding activation entropies, obtained by the least squares method:

$$E_c - E_p = 1209 \pm 1347 \text{ cal/mol}$$

$$\Delta S_c^\ddagger - \Delta S_p^\ddagger = 5.45 \pm 4.12 \text{ cal/K mol}$$

where the confidence limits are at the 95% level.

More recently, one of us^{2,3} has developed a semiempirical method for calculation of the difference $\Delta S_c^\ddagger - \Delta S_p^\ddagger$, which gives values in highly satisfactory agreement with the experimental ones, as obtained by studying the temperature dependence of the free radical cyclopolymerization of divinyl ether and of acrylic anhydride³ and of methacrylic anhydride⁴. When such a method has been applied to evaluate the difference between the activation entropies of reactions (1) (see Appendix), a value of about 20 cal/K mol has been found, well outside the confidence limits of the difference calculated from the experimental¹ r_c values. One might conclude that the procedure followed to calculate $\Delta S_c^\ddagger - \Delta S_p^\ddagger$ is wholly unsatisfactory, in the case of the free radical polymerization of *o*-DVB. It has to be pointed out, however, that even the difference $E_c - E_p$, as obtained from the reported r_c values¹, deserves some comment.

Although no methods are presently available to calculate the difference between the activation energies of an intramolecular cyclization and an intermolecular monomer addition such as reactions (1a) and (1b), it seems reasonable to argue that this difference is primarily influenced by higher conformational energy of the activated complex preceding the ring structure, as compared with the conformational energy of the activated complex of the intermolecular addition. Consequently, one should expect that $E_c - E_p$ is greater the more strained is the ring to be formed. From this point of view it is easily understood that the $E_c - E_p$ differences relative to the free radical cyclopolymerization of acrylic and methacrylic anhydride, in which ring structures endowed with practically the same moderate straining are formed, have been found to be 2.24 kcal/mol³ and 2.25 kcal/mol⁴, respectively. On the other hand, a difference as low as 1.2 kcal/mol between the activation energies of reactions (1) conflicts with the formation of the strained five-membered ring of the indan type structure. These considerations, together with the previous ones on the difference $\Delta S_c^\ddagger - \Delta S_p^\ddagger$, suggest that the cyclopolymerization of *o*-DVB might take place according to a more complicated mecha-

Table 1 Mole fractions f_U of residual unsaturation in the products of the free radical polymerization at 70°C of *o*-DVB at molar concentration [M] in toluene

[M] (mol/l)	f_U	[M] (mol/l)	f_U
0.064	0.293	0.713	0.492
0.116	0.405	1.290	0.542
0.181	0.442	1.621	0.569
0.319	0.456	1.944	0.591

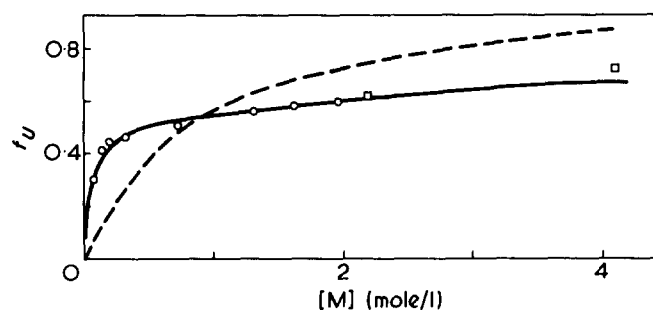


Figure 1 Dependence on monomer concentration [M] of the mole fraction f_U of residual unsaturation in the products of the free radical polymerization at 70°C of *o*-DVB: ○, data of Table 1; □, data reported by Aso¹. - - -, data fitted according to equation (3); —, data fitted according to equation (14)

nism than the one represented by reactions (1). In order to answer this question, the free radical polymerization of *o*-DVB at 70°C has been further investigated. The results so far obtained are reported here.

EXPERIMENTAL

o-Divinylbenzene was prepared by the Wittig synthesis⁵ modified by Maerkl and Merz⁶, by reacting with formaldehyde the phosphorane obtained from *o*-xylylenebis(triphenylphosphonium) bromide which, in turn, was prepared following the procedure reported by Campbell⁷ for *p*-xylylenebis(triphenylphosphonium) chloride. Caustic soda (50%, 50 cm³) was run, under vigorous stirring, into a mixture of *o*-xylylenebis(triphenylphosphonium) bromide (20 g) and methylene chloride (50 cm³). The resulting red solution was reacted with paraformaldehyde (20 g); an exothermic reaction ensued, which was completed in about 15 min. The organic phase was separated off, washed with water, dried and distilled under reduced pressure: *o*-DVB, b.p. 25–82°C (ref 1, b.p. 15–78°C), was obtained in 75% yield. The purity, as checked by gas chromatography, was higher than 99%.

Polymerizations were carried out at 70°C in toluene, in phials sealed under a nitrogen atmosphere. 2,2'-Azobisisobutyronitrile (6.7×10^{-3} mol/l) was used as a free radical initiator. After a polymerization time so selected as to have a monomer to polymer conversion lower than 15%, the phial contents were poured into methanol. The polymer was filtered, washed with methanol to eliminate unreacted monomer, redissolved in toluene and reprecipitated in methanol. The polymer was then dried under vacuum at room temperature. It was completely soluble in benzene, toluene, chloroform and carbon tetrachloride, showing that no cross-links had been formed during the polymerization.

Determination of the residual unsaturation content in the polymers was made following the bromination method already reported⁸.

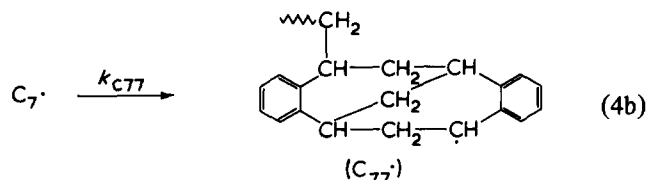
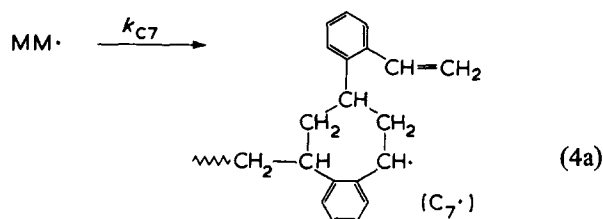
RESULTS AND DISCUSSION

The residual unsaturation values in the products of the free radical polymerization at 70°C of *o*-DVB, expressed as mole fractions, f_U , of monomeric units deriving from monomer molecules which have contributed to the polymer chain growth with only one of their vinyl groups, are collected in Table 1.

On the basis of the chain propagation reactions (1), Aso¹ derived the relationship:

$$f_U = \frac{2[M]}{2[M] + r_c} \quad (3)$$

between the mole fraction of residual unsaturations in the polymers and the monomer concentration [M] at which they were obtained. In Figure 1 (broken line) the data of Table 1, together with those reported by Aso¹ for the free radical polymerization at low monomer to polymer conversion at 70°C of *o*-DVB, are fitted by a non-linear least squares method according to equation (3). It is evidently a rather poor agreement, indicating that the dependence of f_U on [M] is not adequately described by equation (3), and consequently supporting the hypothesis that other chain propagation reactions, besides reactions (1), take place in the free radical polymerization of *o*-DVB. In particular, one might assume that intramolecular cyclization reactions occur, similar in type to those of the bicyclic cyclopolymerization of 1,4-dienes⁹, in which the two last monomeric units entered in the polymer chain are involved, according to the scheme:



In other words, seven-membered rings might be formed which, on the basis of scale models, seem to be endowed with less strain than the five membered rings formed in reaction (1a).

Taking into account reactions (1) and (4), four types of monomeric units can be found in the polymer chains: they are represented in Figure 2. It must be observed that in the bicyclo[4.4.1]undecan structures it would be difficult to distinguish analytically between III and IV monomeric units which, however, differ from a kinetic point of view, being formed through different cyclization reactions. We adopt the convention of labelling as IV the monomeric units which, in these structures, are encountered last when moving end-to-end along the polymer chain.

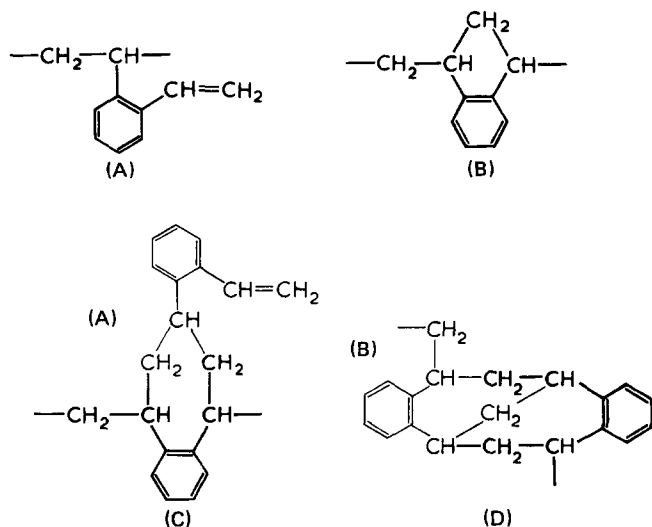


Figure 2 Possible monomeric units in the polymers formed from *o*-DVB

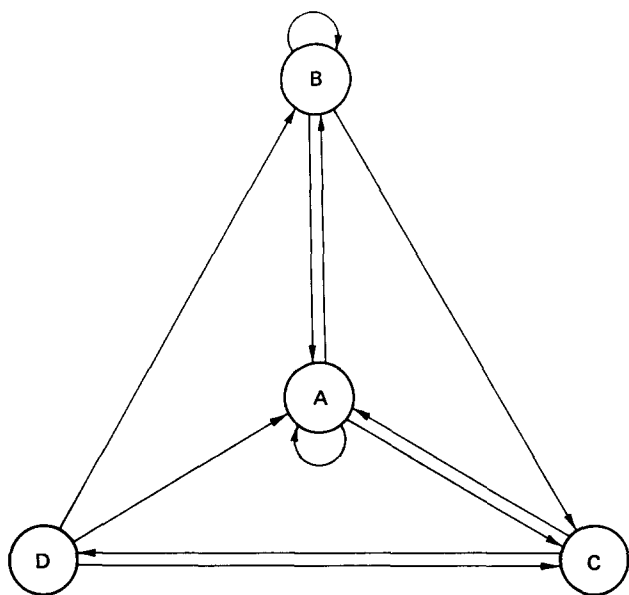


Figure 3 Diagram of the possible transitions between the states of the Markov chain representing a completed macromolecule formed by the monomeric units of Figure 2

In order to derive a relationship between f_U (in the present case, the mole fraction of A monomeric units) and $[M]$, it is convenient to consider the sequence of monomeric units in a completed macromolecule, whose length is so great that the end-groups can be neglected, as the sequence of the four states A, B, C and D of a Markov chain. Taking into account the propagation reactions (1) and (4), it is easy to see that state (monomeric unit) D cannot follow states (monomeric units) A, B or C, and that state C can be followed only by states A or D. This situation is graphically represented in Figure 3, where the arrows indicate the transitions possible between the states. On the basis of Figure 3, and defining as P_{XY} the conditional probability that state X is followed by state Y (X and Y being any one of states A, B, C and D), the probability transition matrix is given by:

$$P = \begin{pmatrix} P_{aa} & P_{ab} & P_{ac} & 0 \\ P_{ba} & P_{bb} & P_{bc} & 0 \\ P_{ca} & 0 & 0 & P_{cd} \\ P_{da} & P_{db} & P_{dc} & 0 \end{pmatrix}$$

Following the procedure described by Price¹⁰, the mole fractions $f_A = f_U$, f_B , f_C and f_D of A, B, C and D monomeric units, respectively, in the chain are given by the co-factor of each element in one column of the determinant $|P - I|$, where I is the unit matrix. Thus:

$$\begin{aligned} f_U = f_A &= \gamma [P_{bb} - 1 + P_{bc}P_{cd}P_{db} - P_{dc}P_{cd}(P_{bb} - 1)] \\ f_B &= -\gamma [P_{ab} + P_{ac}P_{cd}P_{db} - P_{dc}P_{cd}P_{ab}] \\ f_C &= \gamma [P_{ac}(P_{bb} - 1) - P_{ab}P_{bc}] \\ f_D &= -\gamma [P_{ab}P_{bc}P_{cd} - P_{ac}P_{cd}(P_{bb} - 1)] \end{aligned} \quad (5)$$

where γ is a factor which can be cast in terms of the conditional probabilities P_{XY} taking into account that:

$$f_A + f_B + f_C + f_D = 1 \quad (6)$$

Equations (5) can be greatly simplified when the conditional probabilities are expressed through the probabilities that a given growing chain undergoes some sequences of propagation reactions. Making reference to Figure 4, it is easy to see that the probability P_{ja} for a J monomeric unit (J = A, B, C, D) to be followed by a A monomeric unit is given by the product of the probability p_{1m} that a growing chain 1 adds a monomer molecule, and the probability $(1 - p_{mr})$ that the resulting chain radical m does not undergo cyclization to yield r. Since this situation holds true independently of the nature of J, one obtains:

$$P_{aa} = P_{ba} = P_{ca} = P_{da} = p_{1m}(1 - p_{mr}) \quad (7)$$

The probability for J to be followed by a B monomeric unit is simply given, independently of the nature of J, by the probability p_{1n} that a growing chain 1 undergoes cyclization. Thus:

$$P_{ab} = P_{bb} = P_{cb} = P_{db} = p_{1n} \quad (8)$$

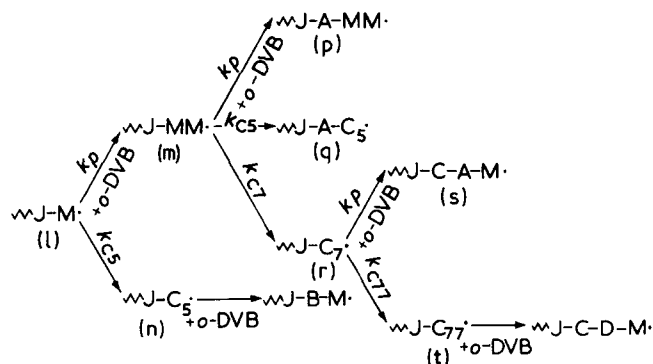


Figure 4 Scheme of the possible chain propagation reactions in the free radical polymerization of *o*-DVB

The probability that a C monomeric unit follows J is given by the probability that 1 adds a monomer molecule, multiplied by the probability that m transforms into r. Thus:

$$P_{ac} = P_{bc} = P_{dc} = p_{1m}p_{mr} \quad (9)$$

Finally, the probability that D follows C is given by:

$$P_{cd} = p_{rt} \quad (10)$$

By introducing (7), (8), (9) and (10) into (5) one obtains:

$$f_U = f_A = \gamma[p_{1n} - 1 + p_{1m}p_{mr}p_{rt}] \quad (11)$$

$$f_B = -\gamma p_{1n}$$

$$f_C = -\gamma p_{1m}p_{mr}$$

$$f_D = -\gamma p_{1m}p_{mr}p_{rt}$$

and taking into account equation (6):

$$\gamma = -\frac{1}{1 + p_{1m}p_{mr}}$$

which can be introduced into equation (11) to give:

$$f_U = p_{1m} \frac{1 - p_{mr}p_{rt}}{1 + p_{1m}p_{mr}} \quad (12)$$

The probabilities p_{1m} , p_{mr} and p_{rt} can be easily expressed in terms of the kinetic parameters. One obtains:

$$p_{1m} = \frac{2[M]}{2[M] + r_5}$$

$$p_{mr} = \frac{r_7}{2[M] + r_5 + r_7}$$

$$p_{rt} = \frac{r_{77}}{2[M] + r_{77}} \quad (13)$$

where $r_5 = k_{C5}/k_p$ is identical to the cyclization ratio r_C of the Aso's equation (3), $r_7 = k_{C7}/k_p$ and $r_{77} = k_{C77}/k'_p$. By introducing equations (13) into (12) one obtains:

$$f_U = \frac{2[M]}{2[M] + r_{77}} \frac{4[M]^2 + 2(r_5 + r_7 + r_{77})[M] + r_5 r_{77}}{4[M]^2 + 4(r_5 + r_7)[M] + r_5(r_5 + r_7)} \quad (14)$$

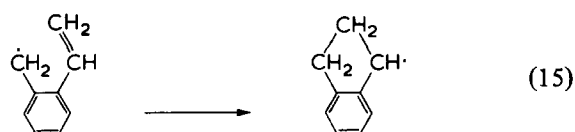
which gives the dependence on monomer concentration of the mole fraction of residual unsaturation in the polymers, when in the chain propagation steps both reactions (1) and (4) take place. Equation (14) reduces to equation (3) when $r_7 = 0$, i.e. when only cyclization reactions yielding indan type structures occur.

By introducing the $[M]$ and f_U values of Table 1 into equation (14), together with the values reported by Aso¹ for the free radical polymerization at 70°C of *o*-DVB at low monomer to polymer conversion, one obtains by a non-linear least square method: $r_5 = 0.08$ mol/l; $r_7 = 7.59$ mol/l and $r_{77} = 0.03$ mol/l. The curve calculated by using these values of the cyclization ratios in equation (14) is compared

in Figure 1 (full line) with the experimental data; a close agreement is apparent, which indicates that the cyclization reactions (4) are very likely to occur in the chain propagation steps of the free radical polymerization at 70°C of *o*-DVB. More specifically, on the basis of the values of the cyclization ratios, reaction (4a) seems to be the most important cyclization process. It has however to be pointed out that at least one of the other cyclization reactions, namely (1a) and (4b), must occur, more significantly at low monomer concentration, since otherwise f_U could not be lower than 0.5 [as one can see by letting $r_5 = r_{77} = 0$ in equation (14)], in contrast with some experimental data of Table 1. The question now arises, if the cyclization ratios taken in consideration in the present paper display a temperature dependence from which an activation entropy difference $\Delta S_c^\ddagger - \Delta S_p^\ddagger$ can be obtained, which agrees with that calculable by the aforementioned procedure^{2,3}. The results of such investigations will be reported in a forthcoming paper.

APPENDIX

The semiempirical method^{2,3} of calculation of the difference $\Delta S_c^\ddagger - \Delta S_p^\ddagger$ between the activation entropies of the intramolecular cyclization and the intermolecular monomer addition occurring in the chain growth steps of a cyclopolymerization process, is essentially based on the hypothesis that the entropy of the activation complex of a chain propagation reaction in free radical polymerization is close to the entropy of the reaction product, and consequently that the activation entropy is similar to the entropy change accompanying the complete reaction. Furthermore, the assumption is made that only the atomic groups which are directly involved in the addition process contribute to the entropy change: specifically, in the case of reactions (1), ΔS_p^\ddagger should be calculated taking into account that in the intermolecular chain propagation reaction the net result is the transformation of a conjugated vinyl group into a $-\text{CH}_2-\text{CH}$ group in the polymer backbone, and ΔS_c^\ddagger should be close to the entropy change accompanying reaction (15) which could be calculated³ if the molar entropies of *o*-methylstyrene and of indan were known.



Unfortunately, only the former is reported¹¹; the entropy of indan, however, can be estimated by a method similar to that applied by Bremner and Thomas¹² according to the group equation:

$$S_{\text{indan}} = S_{\text{benzene}} + S_{\text{cyclopentane}} - S_{\text{ethane}} + R \ln \frac{(\sigma_{\text{benzene}})(\sigma_{\text{cyclopentane}})}{(\sigma_{\text{ethane}})(\sigma_{\text{indan}})} + 1.72 \quad (16)$$

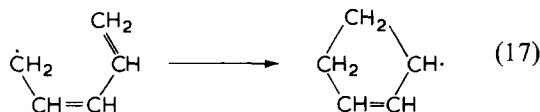
where the S quantities are the molar entropies (in the ideal gas state at 298.16K) of the compounds indicated, the σ 's are the symmetry numbers of their molecules considered as rigid rotators, and the term 1.72 is the internal rotation contribution to the entropy of ethane¹³. Introducing the molar entropies of benzene, cyclopentane and ethane, as obtained from the compilation by Stull, Sinke and Westrum¹¹, to-

gether with the proper symmetry numbers, into equation (16) one obtains:

$$S_{\text{indan}} = 82.59 \text{ cal/K mol}^*$$

With this value and with the one reported¹¹ for the molar entropy of *o*-methylstyrene, one calculates for the activation entropy of reaction (15), according to the procedure described³: $\Delta S_c^\ddagger = -8.54 \text{ cal/K mol}$.

An alternative model for the evaluation of the activation entropy of the cyclization reaction which, according to Aso¹ should take place in the free radical polymerization of *o*-DVB, might be the intramolecular formation of cyclopentenyl radical from pentadienyl radical according to the scheme:



In this case the molar entropies of both 1,3-*cis*-pentadiene and cyclopentene are known¹¹, and one obtains for the activation entropy of reaction (17): $\Delta S_c^\ddagger = -7.70 \text{ cal/K mol}$. The excellent agreement between the activation entropies calculated for reactions (15) and (17) may be taken as an evidence that the procedure followed to estimate the molar entropy of indan gives a reasonable result.

As far as the activation entropy ΔS_p^\ddagger of the intermolecular chain propagation reaction (1b) is concerned, one obtains, according to the method previously reported³:

$$\Delta S_p^\ddagger = S_{\text{C-C}} - (S_{\text{C=C}} - S_{\text{conj}}) + R \ln \sigma \nu + 6.35 \quad (18)$$

* It might be of interest to observe that from the group equation:

$$S_{\text{cyclopentene}} = S_{\text{ethylene}} + S_{\text{cyclopentane}} - S_{\text{ethane}} + R \ln \frac{(\sigma_{\text{ethylene}})(\sigma_{\text{cyclopentane}})}{(\sigma_{\text{cyclopentene}})(\sigma_{\text{ethane}})} + 1.72$$

one calculates: $S_{\text{cyclopentene}} = 68.52 \text{ cal/K mol}$, to be compared with the literature value of 69.23 cal/K mol ¹¹.

where $S_{\text{C-C}}$ is the entropy of a $-\text{CH}_2-\text{CH}_2-$ group in the polymer backbone ($S_{\text{C-C}} = -3.46 \text{ cal/K mol}$ in the present case), $S_{\text{C=C}}$ is the entropy of a vinyl group ($S_{\text{C=C}} = 35.29 \text{ cal/K mol}$), S_{conj} is the entropy decrement due to the conjugation between vinyl and phenyl groups ($S_{\text{conj}} = 1.39 \text{ cal/K mol}$, assuming that the conjugation has the same effect as in the styrene molecule), σ is the symmetry number of the monomer molecule ($\sigma = 2$ for *o*-DVB) and ν is the number of possible conformations of the monomeric unit in the polymer ($\nu = 2$, assuming that no steric control develops during the addition). Therefore one obtained from equation (18):

$$\Delta S_p^\ddagger = -28.25 \text{ cal/K mol}$$

which, together with the previously calculated ΔS_c^\ddagger values, gives a difference of about 20 cal/K mol between the activation entropies of reactions (1a) and (1b).

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