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Solvent effects in copolymerization

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SUMMARY:
Extension of the Mayo-Lewis Model of copolymerization concerning solvent effects in free-radical polymerization is discussed on the basis of the bootstrap and penultimate unit effects.

Much recent experimental work on free-radical copolymerization of vinyl monomers has cast considerable doubt on the validity of the Mayo-Lewis model since it cannot explain all experimental evidence, especially data on rates of copolymerization and the effect of reaction solvents on sequence distribution. The problem now exists to find a proper, hopefully simple way to adapt or extend the Mayo-Lewis model. In doing so, understanding of solvent effects on free-radical polymerization is of paramount importance. In a recent paper Madruga addresses the problem of solvent effects on copolymerization of methyl methacrylate (MMA) and styrene (STY). There is a need for further discussion of the assumptions in this paper that were made to deduce solvent effects on homopolymerization propagation rate constants, $k_p$, and so explain solvent effects on copolymerization.

Madruga began by calculating the ratio $k_t^2/k_i$, $k_i$ representing termination rate constant, from experimentally observed rates of homopolymerization of each of these monomers in three solvents: benzene, chlorobenzene and benzonitrile. He then calculated the values of the termination rate constant, $k_i$, in each solvent by using North's diffusion theory, which assumes a simple inverse proportionality between reaction medium viscosity, $\eta$, and $k_t$.

$$k_i = \frac{k_{i,0}}{\eta}$$

To determine the proportionality constant, $k_{i,0}$, he used literature data for the monomers' termination rate constants in bulk homopolymerization. The values of $k_i,$
so calculated were then used with the experimentally determined ratio $k_p^2/k_i$ to estimate the homopropagation rate constant, $k_p$, in each solvent used. We believe that this combination of experimental and theoretical values may not be accurate enough to quantify the subtle solvent effects in the STY/MMA system.

Madruga's calculation yields the result that $k_p$ is a strong function of solvent, varying by as much as 40% from the values for $k_p$ in the bulk monomers. Few experimental results have previously been published on solvent effects on $k_p$. Among them is the work of Bamford and Brumby for MMA using the rotating sector (RS) in various solvents. Two of us have measured $k_p$ for both STY and MMA using pulsed laser polymerization (PLP) in a few solvents, and have measured by PLP, but not yet published, $k_p$ for MMA in several other solvents. For the solvents in common, the experimental data on MMA available to us are compared to the calculated results in Tab. 1. We note that the RS work showed at 25°C, only a 5% increase for $k_p$ in benzonitrile relative to that in bulk MMA, and a 10 to 20% decrease for chlorobenzene and benzene. This contrasts with a 16 to 40% increase at 60°C calculated by Madruga for these three solvents. The published PLP work showed no effect on $k_p$ for STY in going from bulk monomer to ethylbenzene, or for MMA in going from bulk to ethyl acetate. The unpublished PLP work at 26.5°C has shown much smaller effects of chlorobenzene or benzonitrile on $k_p$ of MMA than Madruga's calculation, and those effects are quantitatively quite consistent with Bamford's results; the unpublished work also shows no effect of chlorobenzene or benzonitrile on $k_p$ of STY. It is important to note that the three data sets are at various monomer concentrations and temperatures, and these different experimental conditions may influence the apparent solvent effects and their differences.

We believe the discrepancies evident in Tab. 1 between experimental measurements and the calculations of $k_p$ from the ratio $k_p^2/k_i$ by Madruga arise from the inaccuracy of Eq. (1), used to estimate $k_i$ in different solvents. In the experimental work demonstrating the effect of $\eta$ on $k_i$ and leading to Eq. (1), North and Reed were careful to choose solvents "all of which might be expected to exhibit similar solvent power towards polymethyl methacrylate". They recognized the importance of isolating viscosity from solvent quality effects: "If the polymer chain extension is independent of the solution viscosity and the various solvents exhibit comparable polymer-solvent interactions, an inverse dependence of the termination rate constant upon solution viscosity must be taken as evidence of a diffusion-controlled reaction". Mahabadi and O'Driscoll have discussed the importance of solvent quality on $k_i$, and shown that not only solvent viscosity, but also the solvent's thermodynamic quality will affect $k_i$, and that a small effect of solvent quality on chain extension can cause a large effect on $k_i$.

It is clear from intrinsic viscosity relations and from solubility parameters that chlorobenzene is a moderately poor solvent for poly(STY). One would therefore predict that solvent quality would tend to increase $k_i$ for STY in chlorobenzene compared to bulk monomer, but viscosity would tend to reduce it. Estimates of $k_i$, using Eq. (1) that do not also take solvent quality effects into consideration will yield incorrect $k_i$ values; coupling these values with valid ratios of $k_p^2/k_i$ will make the $k_p$ estimates in error quantitatively, and the subsequent uses of them may be qualitatively wrong.
Tab. 1. Effect of solvents on propagation rate constant $k_p$ of methyl methacrylate (M)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_p/(L \cdot mol^{-1} \cdot s^{-1})$ from rotating sector$^9$</th>
<th>$k_p/(L \cdot mol^{-1} \cdot s^{-1})$ from pulsed laser polymerization$^7$</th>
<th>$k_p/(L \cdot mol^{-1} \cdot s^{-1})$ from calculation$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(25^\circ C, [M] = 4.69 \text{ mol/L})$</td>
<td>$(26.5^\circ C, [M] = 5.63 \text{ mol/L})$</td>
<td>$(60^\circ C, [M] = 3.0 \text{ mol/L})$</td>
</tr>
<tr>
<td>benzene</td>
<td>260</td>
<td>343.6</td>
<td>374.4</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>330</td>
<td>343.6</td>
<td>374.4</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>280</td>
<td>314.9</td>
<td>815</td>
</tr>
<tr>
<td>bulk$^9$</td>
<td>315.7</td>
<td>314.9</td>
<td>815</td>
</tr>
<tr>
<td></td>
<td></td>
<td>327.5</td>
<td>683.6</td>
</tr>
</tbody>
</table>
The calculated values of $k_p$ were used by Madruga with the experimental copolymerization rate data to examine the effect of three different solvents on the values of the chain end reactivity ratios, $s_1$ and $s_2$. If these $k_p$ values are quantitatively wrong they cannot be used to study the variation of these parameters.

To examine the joint applicability of Fukuda's implicit penultimate unit effect and Harwood's bootstrap models we must recognize that, although Kratochvil et al. suggest that the effect of preferential solvation on kinetic parameters is comparable with experimental error, the experimentally observed bootstrap effect implies that the monomer composition around the growing radicals is solvent dependent and, in a given solvent, may differ significantly from that in bulk. This in turn necessitates that experimentally observed copolymerization parameters are related to the monomer feed composition. Apparent variations of copolymerization parameters may therefore be expected as a function of preferential solvation in a given copolymer/comonomer/solvent system.

In exploring the bootstrap model, Madruga defined two separate partition coefficients, which are reciprocally equal to each other and equivalent to the single partition coefficient as originally defined by Harwood and used in earlier work. In the context of the bootstrap model this partition coefficient is a thermodynamic property, the ratio between comonomer concentrations at the site of propagation and in the bulk of the solution. The partition coefficient can be assigned a value of unity in the bulk system, thus denoting bulk copolymerization as a thermodynamic reference state. This does not mean that the partition coefficient is unity in an absolute sense in bulk copolymerization. The value of the partition coefficient is probably determined by polar effects among solvent, copolymer and comonomers. In recent papers this phenomenon has been incorporated into the quantification of the bootstrap effect by defining the partition coefficient so that it depends linearly on copolymer composition or on some empirical power of comonomer composition ratio.

Further experimental work, clarifying the solvent dependence of rate parameters in copolymerization and the reality of bootstrap and/or penultimate unit effects is obviously needed before we can properly consider a model of copolymerization which can reconcile present anomalies. Any such experimentation must be done with proper consideration of basic principles of model discrimination.

7) T. P. Davis, K. F. O'Driscoll, in preparation