solvent should depend on $V_1(\delta_1-\delta_2)^2$ as $\mu_h=\frac{V_1(\delta_1-\delta_2)^2}{RT}$ where, δ_1 and δ_2 refer to solvent and solvated polymer and R and T are the gas constant and the absolute temperature respectively[3,14]. The δ_2 value does not differ very much from solvent to solvent. If these are of the same type, the value δ_1 will determine the magnitude of the endothermic constituent. If δ_1 is sufficiently different from δ_2, this heat contribution together with μ_s may be large enough to cause μ to exceed its critical value ($\mu_c=0.5$), which is not evident in case of soft and hard segments of shellac resin. Furthermore the δ_s for both the solvents are near to the δ for the shellac and thus the deviation is small in δ and μ values. The above discussion and μ values of shellac segments indicates that no solvation takes place in both the solvents. As in polymers generally initial phase separation occurs when δ_m (solubility parameters of mixture) differ sufficiently from δ_2 the value of the polymers to cause μ to exceed its critical value ($\mu_c=0.5$). Thus this emperical value (μ) of shellac may be used in ascertaining the phase separation in phase separation processes of encapsulation[15–17].

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Letter to Editor

Comments on the kinetic mechanism of free radical bulk copolymerization of styrene–methyl methacrylate*

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The termination mechanism of free radical bulk copolymerization of styrene–methylmethacrylate is chemically controlled as is evident from the literature and the diffusion controlled mechanism postulated by Khan and Wadehra is most likely to be the result of some apparent discrepancies in their experimental data.

Keywords Copolymerization; kinetic mechanism; styrene–methylmethacrylate; **o** factor; polymerization-bulk; polymerization-free radical

In a recent paper published in this journal[1], Khan and Wadehra attempted to reveal the kinetic mechanism of free radical bulk copolymerization of styrene–methylmethacrylate (SMMA). They showed that the parameter φ (which provides a measure of the extent to which termination between unlike radicals is preferred) varies between 127.7 to 20.0 for initiator concentration equal to 0.0076 mol l^{-1} and from 122.3 to 20.24 for initiator concentration equal to 0.0152 mol l^{-1}, when the mole fraction of styrene decreases from 0.871 to 0.365. They concluded that the kinetic mechanism in SMMA copolymerization is governed by diffusion controlled termination and is not chemically controlled even when the conversion is limited to a maximum of 7% and the viscosity of the reaction mass is fairly low. It is the purpose of this communication to show that the conclusions arrived by Khan and Wadehra are contrary to the well accepted kinetic mechanism of chemically controlled termination for SMMA copolymerization.

SMMA copolymerization has been well studied in the literature and at least three different groups[2–4] have

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determined the φ factor by fitting the experimental rates of copolymerization with the theoretical curves (calculated by the well known Mayo–Walling's[5] equation). In the region where the sytrene mol fraction varies between 0.2 to 0.8, there is a close agreement in the values of φ reported by different workers. Indeed it is seen that φ lies in the range 11 to 17, with an average value of φ lying between 13 and 14 as shown (see *Figure 1*). At low styrene concentrations, the theoretical curves lie below the experimental values, while at higher styrene concentrations, the position is reversed. The explanation for the discrepancy is provided by Barb[6] and North and Reed[7]. At higher styrene concentrations the bulk of the radicals with a methylmethacrylate terminal grouping would have a styrene unit as the penultimate group. This group has the effect of enhancing the reactivity of the terminal model to produce an increase in the φ factor[7]. At high concentrations of methylmethacrylate, North and Reed confirm that the termination of the free radical polymerization is diffusion controlled even at viscosities corresponding to that of the monomers.

Recently, while studying the high conversion bulk copolymerization of SMMA, two different groups[8,9] have reported their experimental data at an initial feed composition of 60 mol per cent styrene. At lower conversions (<20 mol%) their experimental rates of copolymerization agrees well with the theoretical rates when the value of φ lies between 13 and 15. The data obtained by Zaitsev *et al.*[10], in their study of copolymerization of SMMA initiated by various peroxides indicate that the initial rates of copolymerization depend on the square root of the initiator concentration.

The conclusions arrived by Khan and Wadehra are thus surprising and are decidedly at variance with the published studies. To probe this discrepancy further, we reporduce the data reported by Khan and Wadehra in *Figure 1*. In the region, where the styrene mole fraction varies from 0.3 to 0.7, the change in the rate of copolymerization reported by two different groups is only about 20% as shown in *Figure 1*, whereas the experimental data of Khan and Wadehra indicates an increase of almost 60%. There is also deviation of about 100% in the relative rates of copolymerization (rate min/rate max) compared with the data of others.

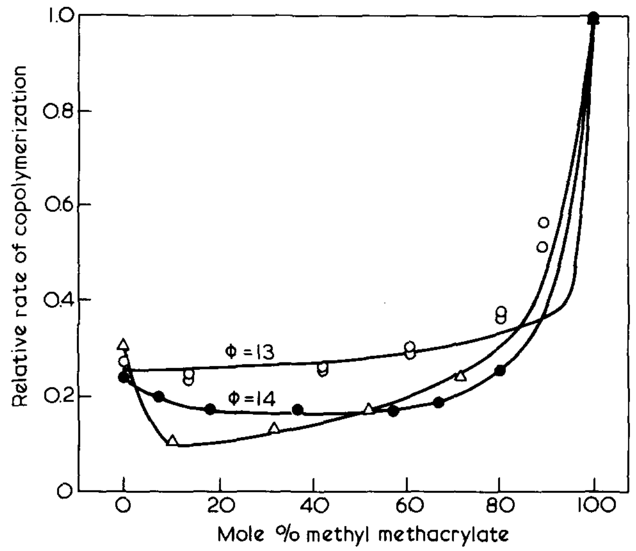

Figure 1 Relative rate of copolymerization as a function of monomer feed composition for styrene–methyl methacrylate. ○, Walling[3]; ●, Melville *et al.*[2]; △, Khan and Wadehra[1]

In summary, we wish to state that chemically controlled termination mechanism of SMMA copolymerization is well proven in the literature and the diffusion controlled mechanism postulated by Khan andWadehra is most likely to be the result of some apparent discrepancies in the experimental data reported by them which have been pointed out above.

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