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Comment on Radical Polymerization Mechanism of Vinyl Benzoate

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Summary

The elementary rate constants for the radical polymerization of vinyl acetate and vinyl benzoate have been determined in various aromatic solvents and ethyl acetate. The k_p values for vinyl benzoate are larger than those for vinyl acetate in all solvents, although methyl affinities of both monomer were similar. These results show that the poly(vinyl benzoate) radical is more reactive than the poly(vinyl acetate) radical.

Introduction

It has long been known that the bulk polymerization rate of vinyl benzoate is far lower than that of vinyl acetate(BURNETT ET AL,1947,1955), although the affinities of both the monomers towards methyl radicals were similar. The low polymerization rate of vinyl benzoate was explained in terms of reversible intramolecular complex between its propagating radical and the aromatic ring(SANTEE ET AL,1964).

We previously determined the elementary rate constants for radical polymerization of vinyl benzoate and vinyl acetate in various aromatic solvents and ethyl acetate, a considerable solvent effect being observed. The solvent effect was explained in terms of donor-acceptor complex between the propagating radical and solvents(KAMACHI ET AL,1978). In this paper, we will compare the propagation rate constants(k_p) for both the monomers in the solvents and show that the low rate of vinyl benzoate is caused by the intermolecular complex rather than the intramolecular complex(SANTEE ET AL, 1964).

Experimental

Vinyl acetate obtained commercially was washed successively with an aqueous 5% $NaHSO_3$ solution, an $NH_2OH{\cdot}HCl$ solution, and water, dried with $CaCl_2$, and then distilled through a Widmer column three times. The fraction distilling at 72-73°C was collected. The sample were degassed, polymerized to the extent of 10% conversion, and the residual monomer was distilled. The purified mon-

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omer was then stored at -78°C until required. Vinyl benzoate was prepared and purified as described in previous paper(KAMACHI ET AL,1978). The rate of polymerization, the rate of initiation and the lifetime of propagating radical were determined as previously described (KAMACHI ET AL,1978).

Results and Discussion

The rate constants obtained are shown in Table 1.

Table 1

The k_p values for vinyl acetate and vinyl benzoate in various solvents at 30°C.

Solvents	VAc, k_p (1/mol·sec)	VBz, k_p (1/mol·sec)
$C_6H_5OCH_3$	48	106
C_6H_6	117	185
C_6H_5F	97	245
C_6H_5Cl	61	168
$C_6H_5COOC_2H_5$	37	69
C_6H_5CN	8	33
$CH_3COOC_2H_5$	637(159)^a	267

( )^a shows the k_p for vinyl acetate in ethyl acetate containing the same concentration of ethyl benzoate as that of vinyl benzoate.

A similar solvent effect on k_p is observed for both the

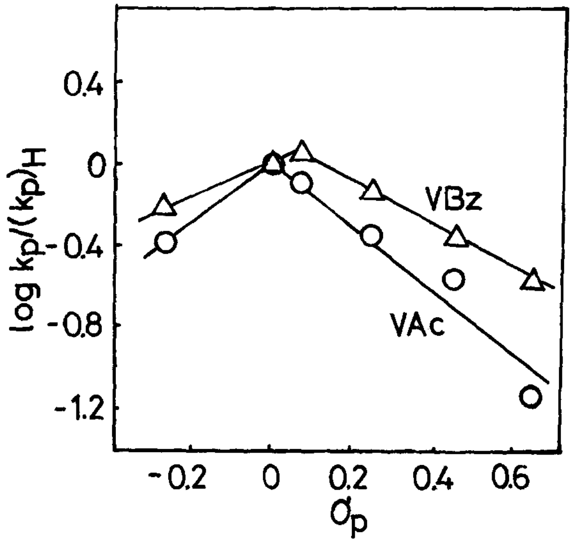

Figure 1 Hammett's plot of solvent effect on k_p values for vinyl acetate and vinyl benzoate.

monomers.(Figure 1) The k_p for vinyl benzoate is larger than that for vinyl acetate in all solvents studied except for ethyl acetate. Since vinyl benzoate has an aromatic ring in itself, the influence of its aromatic ring must be considered in the comparison of k_p in ethyl acetate. Accordingly, k_p for vinyl acetate was determined in ethyl acetate containing the same concentration of ethyl benzoate as that of vinyl benzoate in ethyl acetate. The observed k_p for vinyl acetate(159 l/mol·sec) is smaller than that for vinyl benzoate in ethyl acetate. Thus, it is concluded that k_p for vinyl acetate is smaller than that for vinyl benzoate in all solvents examined. If the propagating radical of vinyl benzoate is stabilized with intramolecular complexation (SANTEE ET AL,1964), k_p for vinyl benzoate would have to be smaller than that for vinyl acetate, because both the monomers have almost the same reactivity toward methyl radicals(SANTEE ET AL,1964). This is not the case. Therefore, the propagating radical of vinyl benzoate is not considered to be more stabilized than that of vinyl acetate, the intramolecular complex mechanism being ruled out for the slow rate of bulk polymerization of vinyl benzoate.

We previously elucidated the solvent effect on k_p for vinyl compounds in terms of the intermolecular complex between the propagating radical and aromatic solvents(KAMACHI ET AL,1977,1978). If it is valid, k_p for vinyl benzoate in bulk polymerization would be similar to that in ethyl benzoate. Since the rate of vinyl benzoate is proportional to the square root of the concentration of initiator as well in bulk as in the presence of solvents(VRACKEN ET AL,1959), the typical radical polymerization in which steady-state assumption is valid is considered to occur even in bulk polymerization. Therefore, $R_p/[M][C]^{0.5}\eta^{0.5}$ for vinyl benzoate was determined in bulk or in the presence of solvents.(Table 2) The ratio of the value in ethyl benzoate to that in benzene or ethyl acetate is in almost accordance with that of the k_p values in the solvents, $R_p/[M][C]^{0.5}\eta^{0.5}$ being proportional to the k_p. Accordingly, $R_p/[M][C]^{0.5}\eta^{0.5}$ in bulk polymerization was compared with that in ethyl benzoate.(Table 2) The fact that $R_p/[M][C]^{0.5}\eta^{0.5}$

Table 2

Comparison of rate of polymerization of vinyl benzoate between bulk and solution.

Solvents	$R_p/[M][C]^{0.5}\eta^{0.5}$
None	4.14×10^{-5}
Ethyl benzoate	4.04×10^{-5}
Benzene	10.0×10^{-5}
Ethyl acetate	16.2×10^{-5}

calculated from the bulk polymerization is almost the same as that in ethyl benzoate also supports that the stabilization of the propagating radical with intermolecular complex is more reasonable than that with intramolecular complex.

Since the propagating radical of vinyl esters were known to be electron-rich(KINOSHITA ET AL,1967), the propagating radicals of vinyl esters were considered to be electron donors to aromatic solvents and the solvent effect on k_p values for vinyl esters were explained in terms of the intermolecular complex between the propagating radical and solvents.(KAMACHI ET AL,1977,1978) If this explanation is true, the propagating radical of vinyl acetate is more electron-rich and the complex formation is expected to be easier in vinyl acetate than in vinyl benzoate, since the methyl group is more electron donating group than the phenyl group. Smaller rate constants of vinyl acetate(Table 1) in all solvents and its larger variation(Figure 1) with solvents than vinyl benzoate give another support to the mechanism of the complex formation between the propagating radical and solvents.

In conclusion, the determination of k_p for vinyl acetate and vinyl benzoate in various solvents indicates that the slow bulk polymerization rate for vinyl benzoate is not due to the intramolecular complex but to the intermolecular complex.

References

1. BURNETT,G.M., and MELVILLE,H.W., Disc. Faraday Soc., 2, 322(1947)
2. BURNETT,G.M., and LOAN,L.D., Trans. Faraday Soc., 51, 214(1955)
3. KAMACHI,M., LIAW,D.J., and NOZAKURA,S., Polymer J., 9, 307(1977)
4. KAMACHI,M., Satoh,J., and NOZAKURA,S., J. Polym. Sci., Polym. Chem. Ed., 16, 1789(1978)
5. KAMACHI,M., LIAW,D.J., and NOZAKURA,S., Polymer preprints, Japan, 27, 708 (1978)
6. KAMACHI,M., LIAW,D.J., and NOZAKURA,S., Polymer Preprints, Japan, 27, 117 (1978)
7. KAMACHI,M. SATOH,J., LIAW,D.J., and NOZAKURA,S., Macromolecules, 10, 501 (1977)
8. KINOSHITA,M., IRIE,T., and IMOTO,M., Makromol. Chem., 110, 47(1967)
9. SANTEE,G., MARCHESSAULT,R.H., CLARK,H.G., KEARNY,J.J., and STANNETT,J., Makromol. Chem., 73, 177(1964)
10. VRANCKEN,A., and SMETS,G., Makromol. Chem., 30 197 (1959)

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