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Preparations and Polymerizations of *p*-Substituted Phenyl Vinyl Sulfides. Vinyl Polymerization 168*

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Summary

p-Substituted phenyl vinyl sulfides (PVS) were prepared and their radical polymerizations were investigated dilatometrically to determine some kinetic constants and to deduce the influences of the sulfur atom and *p*-substituents of PVS. It was found that PVS could be easily homopolymerized by ordinary radical polymerization mechanisms in the presence of 2,2'-azobisisobutyronitrile, contrary to the case of phenyl vinyl ethers, which do not homopolymerize.

From the rates of polymerization (R_p) of PVS and those of *p*-substituted PVS (R_p) under the same conditions, the plot of $\log (R_p/H/R_p/X)$ against the Hammett's equation was found to give a parabola curve. When these results were plotted by the modified Hammett's equation [$\log (k_p X/k_p H) = \rho\sigma + \gamma E_H$], however, a straight line with $\gamma = -4.5$ and $\rho = 0.35$ was obtained. From these results it was concluded that the $3d$ orbital resonance was important in the transition state of the polymerization of these monomers.

The sulfur atom is located in the third row of the periodic table, and has an unoccupied $3d$ orbital which is energetically close to the $3p$ orbital. The sulfur atom is, therefore, quite different from the oxygen atom, which has a similar electron configuration; i.e., the sulfur atom can accept electrons to expand the shell from the octet. Hence the divalent sulfur compounds can operate the electron-accepting conjugation (I).

In the field of organic chemistry, a large number of studies had

* 167: H. Yano, K. Takemoto, and M. Imoto, *J. Macromol. Sci.*, submitted.

been done to compare the behavior of various sulfur compounds and the corresponding oxygen compounds, and the importance of $3d$ orbital conjugation between sulfur and adjacent carbon atoms has been recognized. Particularly, in radical polymerization, some oxygen-containing compounds had been used as monomer, initiator, and so on, whereas sulfur compounds such as mercaptans and disulfides have only been studied systematically as initiators and chain transfer agents (2-8).

Regarding the polymerizations of vinyl sulfide monomers, Price et al. (9,10) prepared PVS, methyl vinyl sulfide, phenyl vinyl sulfone and methyl vinyl sulfone, and then these sulfur compounds were copolymerized with styrene and methyl acrylate to determine their copolymerization parameters. From the results obtained, they emphasized the importance of the $3d$ orbital conjugation of the sulfur atom and the adjacent carbon atom in the transition state. Shostakovskii and co-workers (11) also studied radical and ionic polymerizations of several alkyl vinyl sulfides and PVS.

In this paper, five kinds of unsubstituted and *p*-substituted PVS, such as *p*-methoxy, *p*-chloro, *p*-methyl, and *p*-bromo derivatives were prepared and their bulk homopolymerizations were kinetically investigated to clarify the effect of the sulfur atom and the nuclear substituents in PVS.

EXPERIMENTAL

Preparation of Phenyl Vinyl Sulfide (PVS)

Preparation of Thiophenol. Thiophenol was prepared by the method of Adams and Marvel (12): yield 93-95%.

Preparation of Phenyl-2-hydroxyethyl Sulfide. Phenyl-2-hydroxyethyl sulfide was prepared by the method of Moore et al. (13): yield 90%, b.p. 141°C/11 mm Hg.

Preparation of 2-Chloroethyl Phenyl Sulfide. 2-Chloroethyl sulfide was prepared by the method of Kirner and Richter (14): yield 93%, b.p. 112-114°C/9 mm Hg.

Preparation of PVS. PVS was prepared by the modified method of Montanari (15): 286 g (1.66 moles) of 2-chloroethyl phenyl sulfide was dissolved in 340 ml of ethanol. A solution of 115 g of potassium hydroxide in 700 ml of ethanol was added to the above solution in 1 hr. The mixture was refluxed for 1 hr and then the ethanol

was removed by distillation. The residue obtained was filtered and the precipitate was washed with water. From the filtered solution and the water with which the precipitate was washed, PVS was extracted by ether. After the ether was removed, the residue was distilled under reduced pressure: yield 68.7%, b.p. 60°C/4 mm Hg [lit. (9) 85°C/15 mm Hg], n_D^{25} 1.5866 [lit. (9) 1.5878], d_4^{20} 1.0431 [lit. (9) 1.0386].

Analysis: Found: C, 70.65; H, 6.04; S, 23.33%

Calcd. for C_8H_8S : C, 70.54; H, 5.92; S, 23.54%

Preparation of *p*-Methylphenyl Vinyl Sulfide (CH_3 -PVS)

p-Methylthiophenol was prepared by the method reported by Kramer (16), and CH_3 -PVS was prepared by the same method as in the case of PVS: b.p. 73°C/3 mm Hg [lit. (17) 95°C/10 mm Hg], n_D^{25} 1.5759, d_4^{20} 1.0134.

Analysis: Found: C, 72.08; H, 6.93; S, 21.07%

Calcd. for $C_9H_{10}S$: C, 71.94; H, 6.71; S, 21.34%

Preparation of *p*-Chlorophenyl Vinyl Sulfide (Cl-PVS)

p-Chlorobenzene sulfonyl chloride was prepared by the method of Dumont and Rumpf (18), and Cl-PVS was prepared as the same method as PVS: b.p. 91°C/5 mm Hg, n_D^{25} 1.5992, d_4^{20} 1.1891.

Analysis: Found: C, 56.45; H, 4.27; S, 18.52; Cl, 20.52%

Calcd. for C_8H_7SCl : C, 56.30; H, 4.13; S, 18.79; Cl, 20.77%

Preparation of *p*-Bromophenyl Vinyl Sulfide (Br-PVS)

A very similar method to that used in the preparation of PVS was employed: b.p. 110°C/7 mm Hg, n_D^{25} 1.6250, d_4^{20} 1.4654.

Analysis: Found: C, 44.31; H, 3.45; S, 14.81; Br, 37.31%

Calcd. for C_8H_7SBr : C, 44.67; H, 3.28; S, 14.91; Br, 37.15%

Preparation of *p*-Methoxyphenyl Vinyl Sulfide (CH_3O -PVS)

p-Methoxybenzene sulfonyl chloride was prepared by the method of Muth (19): yield 47.2%. *p*-Methoxythiophenol was pre-

pared by the method similar to that employed in the preparation of thiophenol: yield 62.8%. $\text{CH}_3\text{O-PVS}$ was prepared by the modified method of Reppe (17).

In a 500-ml autoclave was placed a solution of 20 g of potassium hydroxide dissolved in 310 ml of *n*-butanol. To this solution 37.5 g of *p*-methoxythiophenol was added and 22.5 ml of vinyl chloride was introduced into this autoclave. The vessel was kept to react at 160–170°C for 20 hr. Then the mixture was filtered and removed *n*-butanol by distillation under a reduced pressure. $\text{CH}_3\text{O-PVS}$ was obtained by distillation: yield 87%, b.p. 87°C/0.5 mm Hg, n_D^{25} 1.5815, d_4^{20} 1.0993.

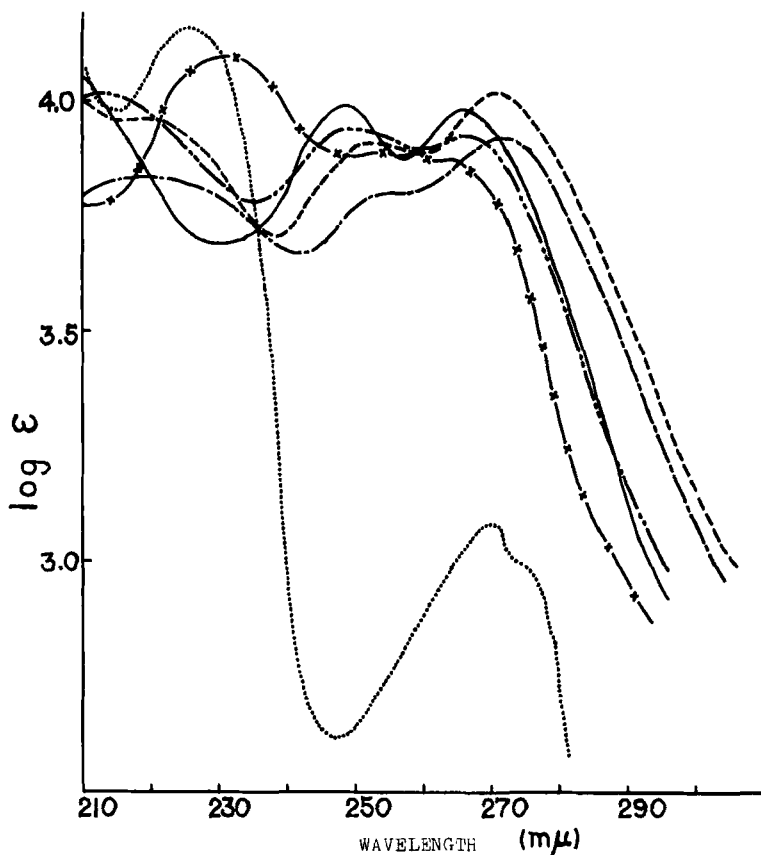


FIG. 1. Ultraviolet absorption spectra of PVS derivatives and phenyl vinyl ether. —, H; ----, Cl; ·····, phenyl vinyl ether; —x—, OCH_3 ; —•—, Br; - - - - , CH_3 . Ethanol solution.

Analysis: Found: C, 65.32; H, 6.25; S, 19.15%
Calcd. for C₉H₁₀SO: C, 65.02; H, 6.06; S, 19.29%

The ultraviolet absorption spectra of these sulfides are shown in Fig. 1.

Initiator and Benzene

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol: m.p. 102.0-102.5°C.

Benzene was obtained by distillation after purification and dehydration from commercial benzene according to the ordinary method.

Polymerization Method

Bulk polymerizations of *p*-substituted PVS were carried out at $30 \pm 0.05^\circ\text{C}$ in dilatometer. The rate of polymerization (R_p) was measured from the shrinkage in the volume of the polymerization mixture.

In the kinetic studies of the polymerization of PVS, the polymerizations were carried out in a sealed tube under shaking in the absence of external light. For determination of effects of monomer concentration on the R_p , benzene-solution polymerization was also done. After polymerization, the contents of the tube were poured into a large amount of methanol to precipitate the polymer. The resulting polymer was thoroughly washed, filtered, and dried under vacuum at room temperature, and then weighed.

The photopolymerizations were performed under the irradiation of a high-pressure mercury lamp (Toshiba SHL-100UV) at 30°C.

RESULTS

Polymerization of Substituted PVS

Figure 2 shows, as an example, the volume shrinkage of the monomer-polymer mixture in the polymerization of PVS. The volume shrinkage ratio of PVS derivatives at 10% conversion are obtained as is shown in Table 1.

The results of the polymerizations of PVS derivatives initiated by AIBN and in the absence of radical initiator are shown in Table 2 and Fig. 3. From Fig. 3, the values of R_p for PVS derivatives were calculated and collected in Table 2.

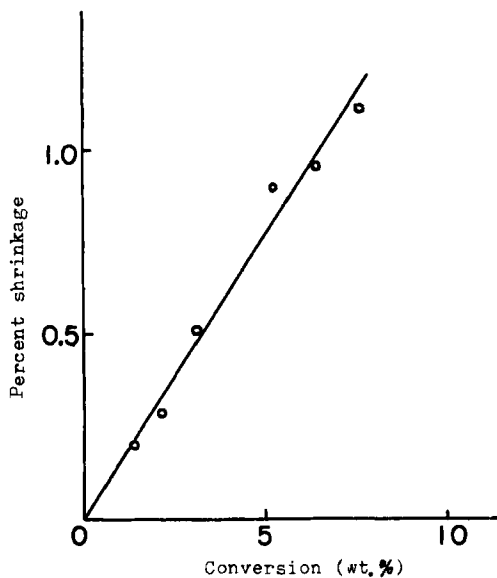


FIG. 2. Volume shrinkage of PVS.

It is observed from Fig. 3 or Table 2 that the unsubstituted PVS polymerizes faster than the substituted PVS.

Determination of Rate Equation for the Polymerization of PVS

Benzene-solution polymerization was carried out to determine the effect of monomer concentration on the R_p , and the concentration of monomer was changed from 1.49 moles/liter to 7.44 moles/liter. In the determination of the effect of initiator concentration,

TABLE I

Volume Shrinkage of PVS Derivatives in Polymerization at 30.0°C

<i>p</i> Substituents in PVS	Volume shrinkage at 10% conversion, %
CH ₃ O	1.33
CH ₃	1.21
H	1.65
Cl	1.08
Br	1.06

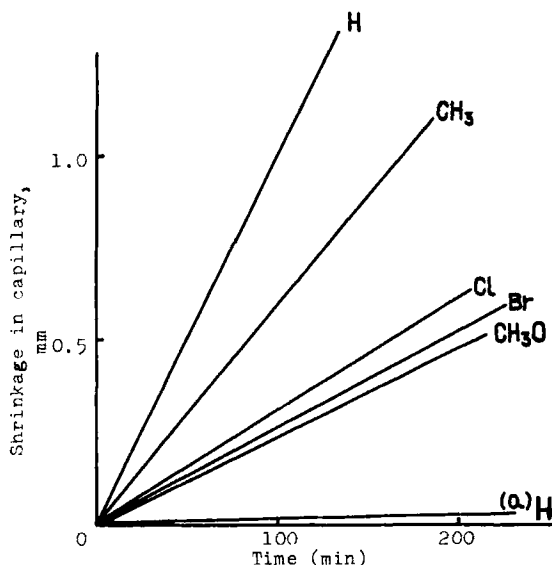


FIG. 3. Rate of bulk polymerization of PVS derivatives initiated by AIBN. [AIBN] = 8.98×10^{-3} mole/liter. (a), [AIBN] = 0.

the concentration of initiator was also changed between 2×10^{-3} mole liter and 10×10^{-3} mole/liter.

The effect of the concentrations of initiator and monomer upon the R_p of PVS at 60°C is shown in Figs. 4 and 5. From these figures it is found that the R_p is proportional to the square-root concentra-

TABLE 2

Rates for Polymerization of Various *p*-Substituted PVS in Bulk Polymerization at 30.0° ([AIBN] = 8.98×10^{-3} mole/liter)

<i>p</i> Substituents in PVS	R_p takes place $\times 10^6$, moles/liter-sec	Overall rate constant ($k \times 10^6$), ^a moles/liter-sec
CH ₃ O	0.490	0.790
CH ₃	1.42	2.24
H	1.98	2.79
Cl	0.829	1.82
Br	0.698	1.09

^a Calculated from Eq. (1).

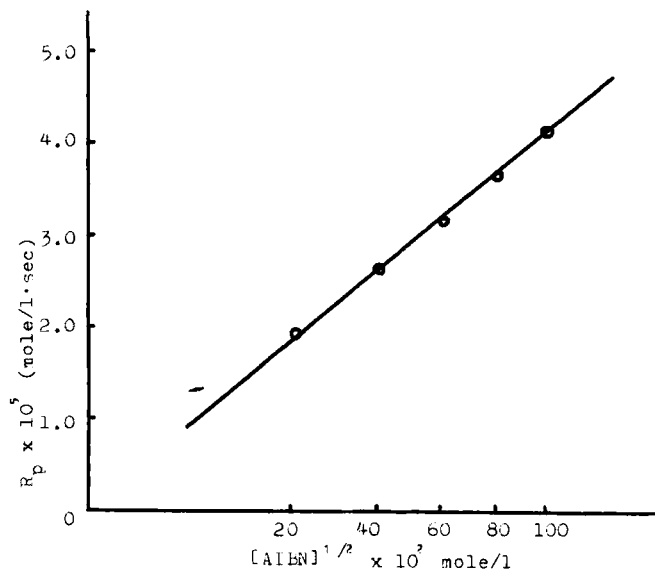


FIG. 4. Relationship between the rate of polymerization and the concentration of initiator at 60°C ($[PVS] = 7.44$ mole/liter).

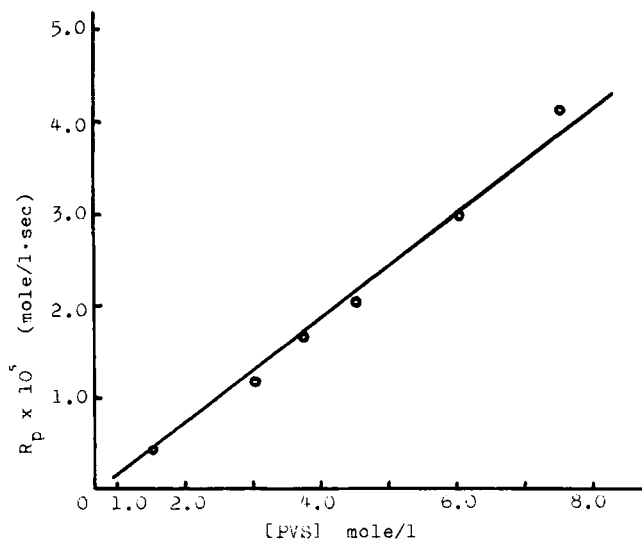


FIG. 5. Relation between the rate of polymerization and the monomer concentration at 60°C ($[AIBN] = 1.0 \times 10^2$ mole/liter).

tion of the initiator, and is also directly proportional to the concentration of the monomer, as shown by

$$R_p = k[\text{AIBN}]^{1/2}[\text{PVS}] \quad (1)$$

This result suggests that the polymerization of PVS proceeds with the ordinary radical polymerization mechanism.

Determinations of Activation Energy and Entropy

A plot of $\log R_p$ against $1/T$ according to the Arrhenius' equation is shown in Fig. 6 and Table 3, from which the overall activation energy was obtained as 21.4 kcal/mole.

The frequency factor (A) was calculated as 3.09×10^8 from the values of activation energy and the overall polymerization rate constant (k). Activation entropy was also calculated from these values, $\Delta S^\ddagger = -10.2$ eu.

Photopolymerization of CH_3 -PVS

Figure 7 shows the results obtained from the photopolymerization of CH_3 -PVS. The rates of photopolymerizations, in the presence and absence of AIBN as a photosensitizer, were 12.7 and 10.3

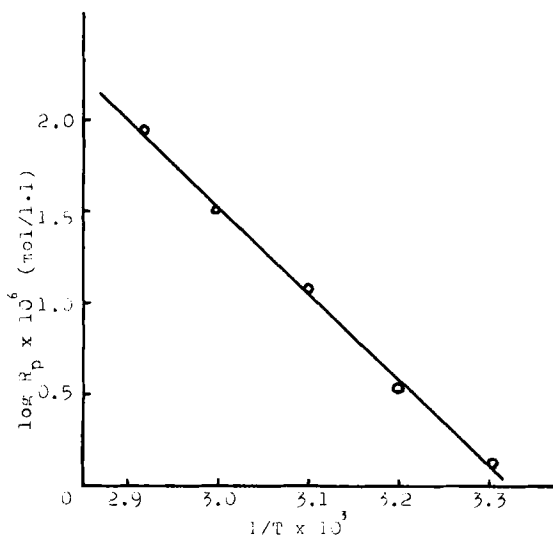


FIG. 6. Relation between the rate of polymerization and $1/T$.

TABLE 3

Results of Bulk Polymerization of PVS at Different Temperatures
 ($[AIBN] = 7 \times 10^{-3}$ mole/liter)

Temp., °C	Rates of polymerization, moles/liter-sec
30	1.29×10^{-6}
40	3.42×10^{-6}
50	1.13×10^{-5}
60	3.28×10^{-5}
70	8.94×10^{-5}

times larger than those of thermal polymerization. From this result, PVS itself was considered to act as a photosensitizer.

DISCUSSION

Although phenyl vinyl ether (PVE) does not homopolymerize in the presence of radical initiator, PVS and its derivatives can homopolymerize under the similar conditions. From the observed rate

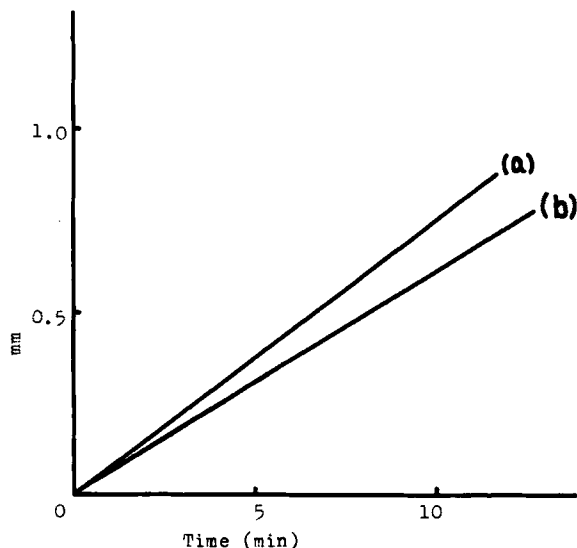
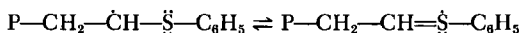


FIG. 7. Rate of polymerization of *p*-methylphenyl vinyl sulfide (photopolymerization at 30°C). (a), AIBN photosensitizer: $[AIBN] = 8.98 \times 10^{-3}$ mole/liter; (b), photosensitizer: none.

Eq. (1), it is obvious that this polymerization proceeds with the ordinary radical mechanism.

When comparing the kinetic constants for the polymerization of PVS with those of styrene, little difference is observed. The rate of polymerization of PVS is about $\frac{1}{2}$ that for styrene under similar conditions.

As may be seen from Fig. 1, ultraviolet spectra of PVS and its derivatives are shifted to a longer wavelength than that of PVE. It is known that this result corresponds to the difference between the $2p$ - $3p$ conjugation of the sulfur and adjacent carbon atoms in PVS and the $2p$ - $2p$ conjugation of oxygen and adjacent carbon atom in PVE (1,20). Since the $2p$ - $3p$ conjugation of PVS is weaker than the $2p$ - $2p$ conjugation of PVE, it may be said that the $2p$ - $2p$ conjugation of PVE is too stable to react with a radical. In the ground state of PVS, however, the $2p$ - $3p$ conjugation is not so stable, and the new electron-sharing conjugation caused by the $3d$ orbital of the sulfur atom in PVS may have participated in the transition state of its polymerization.



Such stabilization by $3d$ orbital resonance in PVS radical is supported from its observed Q value (0.35) reported by Price and also by us (21).

To deduce the effect of p substituents of PVS, relative rates of polymerization as indicated in Table 2 were plotted with the Hammett σ constants of the p substituents. This result is shown in Fig. 8, from which it is noted that this plot gives a parabola curve, showing the maximum at the unsubstituted PVS. Imoto and co-workers (22) reported that a similar correlation was observed between the termination rate constant of radical polymerization of p -substituted styrenes and the σ constants of their p substituents.

Recently, the following modified Hammett's equation was presented by Yamamoto and Otsu (23) and was found to be good applicability for many radical reactions:

$$\log(k/k_0) = \rho\sigma + \gamma E_R \quad (2)$$

where σ and E_R are the Hammett polar substituent constant and the resonance substituent constant of p substituents, and γ and ρ are reaction constants. When the results of Table 2 were plotted by Eq. (2), a straight line was obtained as $\rho = 0.35$ and $\gamma = -4.5$, as is shown in Fig. 8.

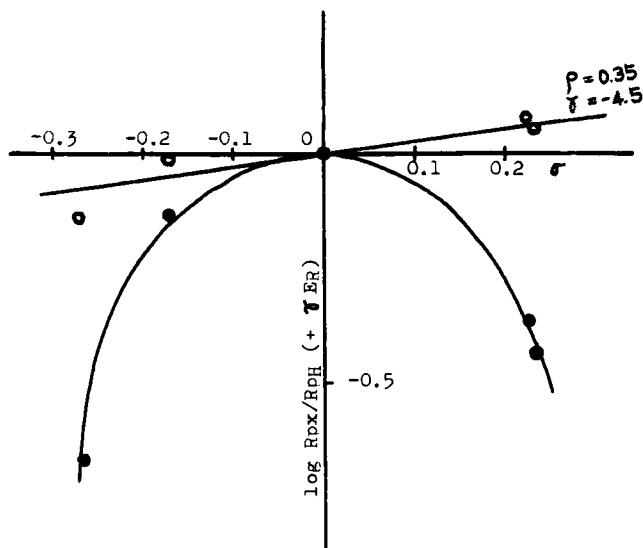


FIG. 8. Relationship between the rate of polymerization and Hammett's σ constant. (●), plotted by Hammett's equation; (○), plotted by Eq. (2).

From the values of ρ and γ obtained, it may be said that both polar and resonance effects of the p substituents in PVS are important for the radical polymerization of these monomers.

REFERENCES

1. C. C. Price and S. Oae, *Sulfur Bonding*, Ronald Press, New York, 1962.
2. T. Otsu, *J. Polymer Sci.*, **21**, 559 (1956).
3. T. Otsu, Nayatani, I. Muto, and M. Imai, *Makromol. Chem.*, **27**, 142 (1958).
4. T. Otsu and K. Nayatani, *Makromol. Chem.*, **27**, 149 (1958).
5. T. Otsu and H. Motooka, *Kogyo Kagaku Zasshi*, **62**, 287 (1959).
6. K. Tsuda, S. Kobayashi, and T. Otsu, *Bull. Chem. Soc. Japan*, **38**, 1517 (1965).
7. T. Ferington and A. V. Tobolsky, *J. Am. Chem. Soc.*, **8**, 3215 (1958).
8. W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962).
9. C. C. Price and H. Morita, *J. Am. Chem. Soc.*, **75**, 4747 (1953).
10. C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, **72**, 14 (1950).
11. N. F. Shostakovskii, E. N. Prilezkaeva, and V. N. Karavaeva, *Vysokomolekul. Soedin.*, **1**, 781 (1959).
12. R. Adams and C. S. Marvel, *Organic Syntheses*, Collection Vol. I, 1956, p. 504.
13. A. H. F. Moore, R. A. Peters, and R. W. Wakelin, *J. Chem. Soc.*, **1949**, 1755.
14. W. R. Kirner and C. H. Richter, *J. Am. Chem. Soc.*, **51**, 3413 (1929).
15. F. Montanari, *CA*, **51**, 5723b (1957).
16. H. J. Kramer, *Rec. Trav. Chim.*, **53**, 1102 (1934).

17. W. Reppe et al., *Ann.*, **601**, 81 (1956).
18. J. M. Dumont and P. Rumpf, *Bull. Soc. Chim. France*, **1962**, 1213.
19. F. Muth, in Hauben-Weyl, 4 Aufl., **9**, 576 (1955).
20. M. Hirota, *Physical Methods in Organic Chemistry*, Vol. 1, Kyoritsu, 1965, p. 25.
21. K. Tsuda, S. Kobayashi, and T. Otsu, unpublished data, 1966.
22. M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **86**, 217 (1965).
23. T. Yamamoto and T. Otsu, *Chem. Ind.*, **1967**, 787.

Zusammenfassung

p-Substituierte Phenylvinylsulfide (PVS) wurden dargestellt wobei deren Polymerisation dilatometrisch untersucht wurde um einige kinetische Konstanten zu bestimmen und daraus den Einfluss von Schwefelatomen und p-substituenten im PVS abzuleiten. Es wurde gefunden, dass PVS sich leicht nach gewöhnlichen Radikalpolymerisationsmechanismen homopolymerisieren lässt in Gegenwart von 2,2'-Azodiisobuttersäurenitril. Dies steht im Gegensatz zu Phenylvinyläther, der nicht homopolymerisiert werden konnte.

Aus den Polymerisationsgeschwindigkeiten (R_pH) von PVS und von p-substituierten PVS (R_pX) bei denselben Bedingungen ergab sich eine parabolische Kurve, wenn man $\log(R_pH/R_pX)$ gegen die Hammett Gleichung aufrägt. Wenn dieselben Daten nach der modifizierten Hammett Gleichung aufgetragen wurden [$\log(k_pX/k_pH) = \rho\sigma + \gamma E_R$], ergab sich jedoch ein Gerade für $\gamma = -4.5$ und $\rho = 0.35$. Auf Grund dieser Ergebnisse wurde gefolgert, dass die 3d Orbitalresonanzen eine wichtige Rolle für den aktivierten Zustand bei der Polymerisation dieser Monomeren spielen.

Résumé

On a préparé et étudié par dilatométrie la polymérisation radicalaire des sulfures de phényl vinyl (PVS), dans le but de déterminer quelques constantes cinétiques et pour en déduire l'influence de l'atome du soufre et des substituants para de PVS. On a trouvé que le PVS peut facilement homopolymériser par un mécanisme radicalaire ordinaire en présence du 2,2'-azobisisobutyronitrile, contrairement à l'éther phényl vinylique qui n'homopolymérise pas.

On a trouvé à l'aide des vitesses de polymérisation (R_pH) du PVS et des PVS substitués en para (R_pX) dans les mêmes conditions, que la courbe du $\log(R_pH/R_pX)$ contre l'équation de Hammett donne une parabole. Lorsqu'on a tracé ces résultats avec l'équation modifiée de Hammett [$\log(k_pX/k_pH) = \rho\sigma + \gamma E_R$] une ligne droite est obtenue avec $\gamma = -4.5$ et $\rho = 0.35$. De ces résultats on a conclu que la 3d résonance orbitale joue un rôle important dans l'état de transition lors de la polymérisation de ces monomères.

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