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# SYNTHESIS, POLYMERIZATION, AND COPOLYMERIZATION OF VINYL THIOACETATE*

G. HARDY, J. VARGA, K. NYTRAI, I. TSAJLIK and L. ZUBONYAI

Scientific Research Institute for the Plastics Industry, Budapest; Budapest Polytechnic Institute

THE results of radiobiological investigations have shown that mercaptoamino derivatives such as 4-mercaptobutylamine, 3-mercaptopropylamine [1], 1-mercaptopropylamine, and 2-mercaptopropylamine [2], and their derivatives, reduce the harmful effect of radiation on living organisms and are effective protective agents against radiation.

To alter some of the undesirable properties of low-molecular-weight mercapto compounds (unpleasant odours, rapid elimination from the organism) Overberger *et al.* [3, 4] have synthesized polymers containing a mercapto group which are also effective protective agents againts radiations.

It appeared to be of interest to synthesize macromolecules similar to the mercaptoamino compounds mentioned above. Since the corresponding monomers (vinylamine, vinyl mercaptan) are chemically unstable compounds, polymers
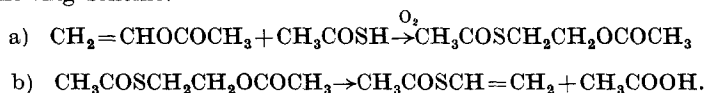
containing free amino and mercapto groups proved to be capable of synthesis only indirectly. The chemical conversion of copolymers of vinyl thioacetate and N-vinyl compounds proved to be possible.

In our work, we have investigated the conditions of obtaining vinyl thioacetate (VTA), the features of its homopolymerization and copolymerization, and the possibility of subjecting the polymers obtained to chemical transformations. In copolymerization, the comonomers used were certain N-vinyl compounds, such as N-vinylsuccinimide (VSI), N-vinylphthalimide (VPI) and N-vinylcarbazole (VC). The conditions for obtaining copolymers containing free mercapto and amino groups from VTA and VSI and from VTA and VPI have been investigated.

## EXPERIMENTAL

*Synthesis of VTA.* The VTA was synthesized by a patent procedure [5] in accordance with the following scheme:

a) $\quad CH_2=CHOCOCH_3 + CH_3COSH \xrightarrow{O_2} CH_3COSCH_2CH_2OCOCH_3$

b) $\quad CH_3COSCH_2CH_2OCOCH_3 \rightarrow CH_3COSCH=CH_2 + CH_3COOH.$

*2-Acetoxyethyl thioacetate.* A round-bottomed flask fitted with a reflux condenser and a gas-inlet tube was charged with 86 g (1 mole) of freshly distilled vinyl acetate and 100 g of thioacetic acid. Air was passed slowly through the reaction mixture until the evolution of heat ceased ($\sim 1$ hour.) The unchanged thioacetic acid was distilled off in vacuum (50 mm), and the 2-acetoxyethyl thioacetate was distilled at 10 mm. The yield was $\sim 100\%$; b.p. 103–105/10 mm; $d_{25}$ 1·1382, $n_D^{25}$ 1·4737; $MR_D$: found 39·87; calculated 39·77.

*VTA* was obtained by the pyrolysis of the 2-acetoxyethyl thioacetate in a current of $CO_2$ in an iron tube 75 cm long and 5 cm in diameter filled with Raschig rings and provided with an electric heater. Under the given conditions, the optimum parameters of the pyrolysis were as follows: temperature 490°, rate of flow 50 g/hour, velocity of the carrier gas 20 l./hour. The reaction product was shaken first with water and then with $NaHCO_3$. The organic layer was separated off and dried with calcined $Na_2SO_4$, and then the fractions boiling up to 80° at 100 mm were distilled off. The resulting product was rectified under atmospheric pressure. The yield of VTA was 25–28%; b.p. 121–123°; $d_{25}$ 1·0158; $n_D^{25}$ 1·4920.

Attempts to synthesize VTA by the direct vinylation of thioacetic acid were unsuccessful. Catalysts used were mercuric acetate and a mixture of it with boric acid and zinc sulphate. No reaction took place under the influence of UV light, either.

*VSI and VPI* were synthesized as described by Nikolayev and Ushakov [6]. The technical VC that we had available was purified by recrystallization from benzene.

The kinetic measurements were carried out by the dilatometric method using azoisobutyronitrile (AIBN) as the initiator in an atmosphere of nitrogen. Because of its comparatively low value, the determination of the molecular weight of the poly-(vinyl thioacetate) was carried out by the cryoscopic method in benzene. The molecular weight of the poly-(vinyl acetate) was determined by the viscosimetric method [7].

In the study of copolymerization, sealed tubes containing 15 g of material were used; the reaction was carried out at 60°. AIBN was used as the initiator. The copolymerization experiments were carried out in bulk with the exception of some experiments with VPI which were carried out in benzene solution, the concentration of VPI amounting to from 0·7 to 0·8 as a molar fraction of the initial mixture of monomers. Copolymerization was stopped at a low conversion and the reaction mixture was diluted with dimethylformamide.

The copolymers obtained were purified by twofold reprecipitation. Where the content of VTA was large, the VTA–VSI and VTA–VPI systems were precipitated with ether (the copolymer swelled considerably and precipitated in the form of clots), but precipitation was repeated from benzene solution with petroleum ether. When the content of VTA in the VTA–VSI and VTA–VPI system was low, methyl alcohol was used to precipitate the copolymers. The VTA–VS copolymers were twice reprecipitated from solution in dimethylformamide with methyl alcohol. The compositions of the copolymers were determined from their nitrogen contents.

## RESULTS AND DISCUSSION

*Polymerization of VTA.* Figure 1 shows the results of kinetic measurements at various initial concentrations of the initiator (the numbers of the curves correspond to the numbers of the experiments in the numerical data given below).
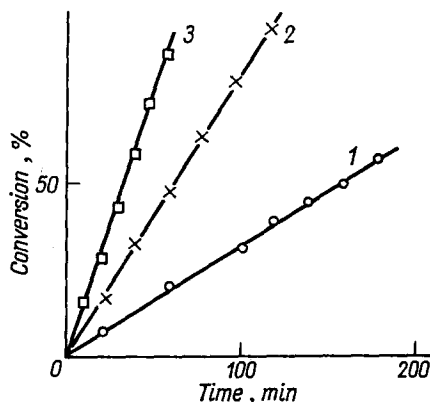


FIG. 1. Kinetics of the polymerization of vinyl thioacetate at various concentrations of initiator. The numbers on the curves correspond to the numbers of the experiments.
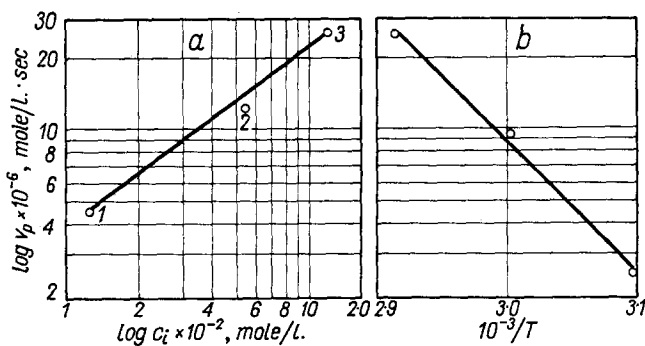


FIG. 2. Rate of polymerization of vinyl thioacetate as a function of: *a*—concentration of initiatior at 60°; *b*—the temperature.

Figure 2*a* shows the velocity of polymerization as a function of the concentration of initiator. In can be seen from the experimental results that the velocity of polymerization is proportional to the concentration of initiator to the power

of 0·75. The influence of the temperature on the rate of polymerization is shown in Fig. 2b; the over-all activation energy calculated from this is 25·45 kcal/mole, which is an overestimated figure. The mean polymerization coefficient of the poly-(vinyl thioacetate) (PVTA) depends on the concentration of initiator to an extremely small extent.

The dependence of the molecular weight on the concentration of the azo-isobutyronitrile at 60° is expressed by the following numerical data:

| Experiment No. | 1 | 2 | 3 |
|---|---|---|---|
| Concentration of initiator, mole/l. $\times 10^2$ | 1·266 | 5·426 | 12·01 |
| Molecular weight | 1723 | 1559 | 1369 |
| Degree of polymerization | 17 | 15 | 13 |

A similar phenomenon may be observed with polymers for which a high velocity constant of chain transfer by the monomer is characteristic (for example, vinyl acetate, vinyl chloride, allyl derivatives). In actual fact, for VTA the chain-transfer constant for the monomer $C_M$ is high; calculated from the data of Fig. 3 it is 0·056 at 60°. For comparison, Table 1 shows the chain-transfer constant of the monomers for some vinyl ethers.
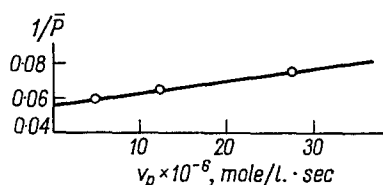


FIG. 3. Polymerization coefficient of poly-(vinyl thioacetate) as a function of the rate of polymerization at 60°.

TABLE 1. CHAIN-TRANSFER CONSTANT OF THE MONOMER ($C_M$) FOR SOME VINYL ESTERS

| Monomer | Tempera- ture, °C | $C_M \times 10^3$ | Litera- ture reference |
|---|---|---|---|
| Vinyl thioacetate | 60 | 56 | — |
| Vinyl acetate | 60 | 0·15 | [8] |
| Vinyl pelargonate | 60 | 1·5 | [8] |
| Vinyl stearate | 60 | 2·3 | [8] |
| Vinyl benzoate | 79·6 | 0·7 | [9] |
| Vinyl salicylate | 70 | 8·0 | [10] |

It can be seen from these results that the chain-transfer constant of VTA is extremely high. This can apparently be explained by the presence of the thioester group. Since we have been unable to find values of the chain-transfer

constans for thioesters in the literature, for confirmation we have determined the chain-transfer constant for a saturated thioester—2-acetoxyethyl thioacetate (AETA) in the polymerization of vinyl acetate (VAc). As can be seen from
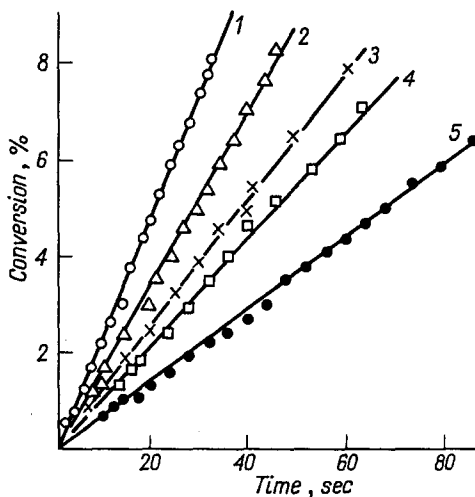


FIG. 4

FIG. 5

FIG. 4. Kinetics of the polymerization of vinyl acetate in the presence of 2-acetoxyethyl thioacetate at 60°. The numbers on the curves correspond to the numbers of the experiments in Table 2.
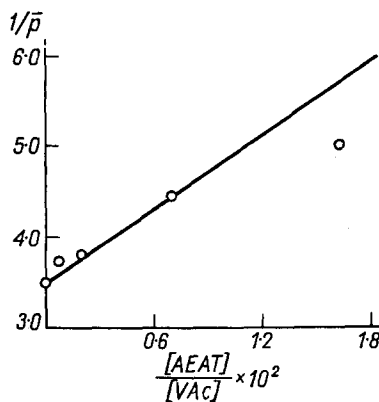
FIG. 5. Molecular weight of poly-(vinyl acetate) as a function of the concentration of 2-acetoxyethyl thioacetate.

Fig. 4, AETA inhibits the polymerization of VAc and reduces the polymerization coefficient of the polymers formed (Table 2).

TABLE 2. POLYMERIZATION OF VINYL ACETATE (VAc) IN THE PRESENCE OF 2-ACETOXYETHYL THIOACETATE AETA AT 60°

| Experiment No. | Concentration, mole/l. | | AIBN mole/l. × $\times 10^3$ | $\dfrac{[AETA]}{[VAc]} \times 10^3$ | $[\eta]$ | $\dfrac{1}{P} \times 10^4$ |
|---|---|---|---|---|---|---|
| | VAc | AETA | | | | |
| 1 | 10·34 | — | 1·54 | — | 1·44 | 3·46 |
| 2 | 10·33 | 0·00905 | 1·54 | 0·876 | 1·36 | 3·70 |
| 3 | 10·31 | 0·02104 | 1·54 | 2·040 | 1·34 | 3·76 |
| 4 | 10·20 | 0·0735 | 1·52 | 7·210 | 1·17 | 4·41 |
| 5 | 10·03 | 0·1652 | 1·50 | 16·500 | 1·06 | 4·93 |

The chain-transfer constant of AETA in the polymerization of VAc at 60°, calculated from the results of Fig. 5, is approximately $1·32 \times 10^{-2}$. This value is close to the chain-transfer constant of VTA and is approximately two orders

of magnitude greater than the chain-transfer constants of ordinary esters. (Thus, for example, according to Vensheidt and Hardy's results [11], in the polymerization of VAc at 70° the chain-transfer constant of the VAc is $1.81 \times 10^{-4}$ and that of allyl acetate is $7.23 \times 10^{-4}$.

*Copolymerization of VTA with N-vinyl compounds.* In the polymerization of mixtures of VTA with the N-vinyl compounds that we investigated, copolymers are formed and not mixtures of homopolymers. This was confirmed by the fact that the copolymers obtained are soluble in benzene and contain nitrogen.

Figures 6*a*, *b* and *c*, illustrates the composition of the polymers formed as a function of the composition of the initial mixture of monomers at a low conversion. By means of Fineman and Ross's equation [12]
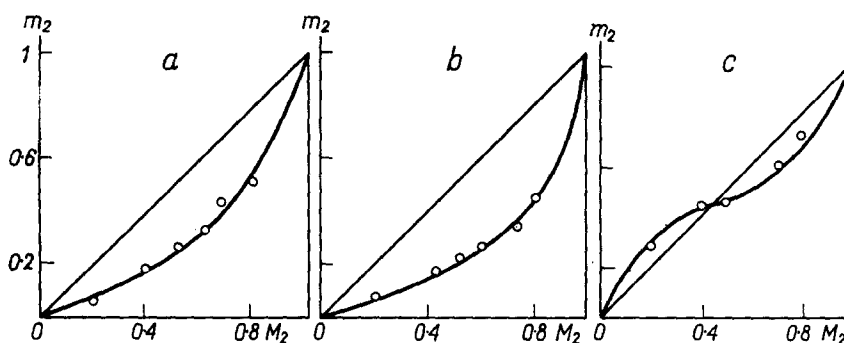
$$(f-1)/F = (f/F^2)\, r_2 + r_1$$



FIG. 6. Relationship between the compositions of the initial mixture and the copolymer obtained: *a*—for vinyl thioacetate and N-vinylsuccinimide; *b*—for vinyl thioacetate and N-vinylphthalimide; *c*—for vinyl thioacetate and N-vinylcarbazole.

(where $F = M_1/M_2$ and $f = m_1/m_2$, $M_1$ and $M_2$ being the molar fractions of the monomers in the initial mixture, and $m_1$ and $m_2$ being the molar fractions of the monomers in the copolymer) we have calculated from our results the copolymerization constants $r_1$ and $r_2$ (Figs. 7*a*, *b* and *c*) given in Table 3

For comparison, the table also gives the values of $r_1$ and $r_2$ in the copolymerization of the N-vinyl compounds mentioned above with VAc from literature data [13–16]. It can be seen from the table that the N-vinyl compounds are more active than VAc, VTA is more active than VSI and VPI, and VC is a monomer of medium activity. Consequently, replacing oxygen by sulphur greatly increases copolymerization activity. To specify the tendency of VTA to undergo copolymerization, Alfrey and Price's magnitudes $Q$ and $e$ were determined using the values of $Q$ and $e$ known from the literature for VSI [16] and VC [17]. The values of $Q$ and $e$ for VTA calculated from the results for VSI are 1·67 and $-1.3$, respectively and those calculated from the data for VC are 1·75 and $-2.28$. As is well known, the value of $Q$ depends on the conjugation of the double bond of the monomer with the substituent present on the double bond and the magni-

tude of $e$ expresses the electron-donating or electron-accepting capacity of the substituents [18]. By comparing the values of $Q$ and $e$ for VTA and VAc ($Q_{VAc}=$ 0·028, $e_{VAc}=-0·30$) it can be established that the replacement of oxygen by sulphur increases $Q$ for the monomer but displaces $e$ into the region of negative
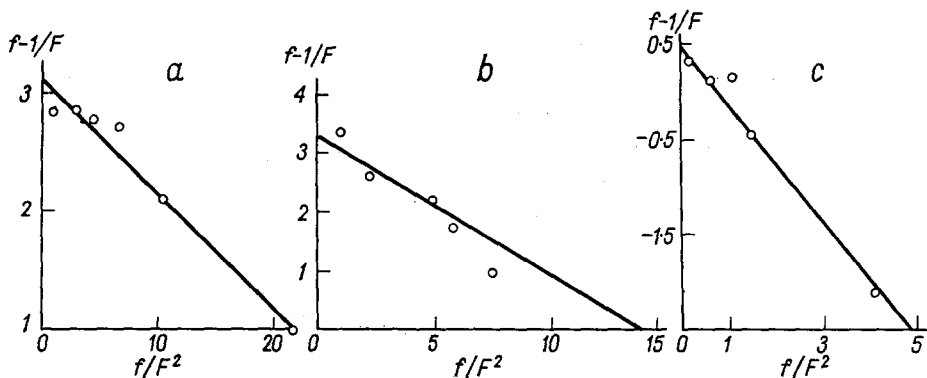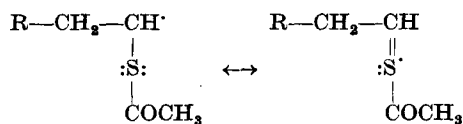


FIG. 7. Fineman-Ross diagram for the copolymerization of vinyl thioacetate with: $a$—N-vinylsuccinimide; $b$—N-vinylphthalimide; $c$—N-vinylcarbazole.

TABLE 3. COPOLYMERIZATION CONSTANTS OF VINYL THIOACETATE
AND VINYL ACETATE WITH VARIOUS N-VINYL MONOMERS

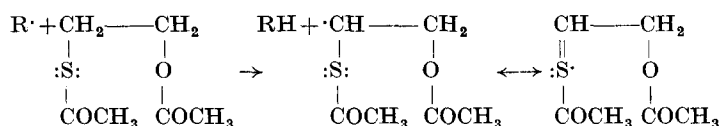| Monomer $M_2$ | Monomer $M_1$ | | | |
| --- | --- | --- | --- | --- |
| | VAc* | | VTA | |
| | $r_1$ | $r_2$ | $r_1$ | $r_2$ |
| N-Vinylsuccinimide | 0·07 | 2·4 | 3·1 | 0·095 |
| N-Vinylphthalimide | 0·18 | 2·08 | 3·2 | 0·23 |
| N-Vinylcarbazole | 0·126 | 6·05 | 0·5 | 0·622 |

* Temperature of copolymerization 65°.

values. Such a large negative value of $e$ can be explained by the fact that the electron-donating properties of sulphur are stronger than those of oxygen. The relatively high value of $Q_{VTA}$ in comparison with $Q_{VAc}$ can be explained by the fact that the electrons of the $\pi$-bond participate in conjugation with the $d$-orbital of the sulphur atom ($\pi-d$ conjugation). The free radicals obtained from VTA are more stable than the VAc radicals, since the expansion of the unpaired electron into the $d$-orbital of the sulphur atom gives rise to the following possibility of resonance stabilization [19]:

$$R—CH_2—CH \cdot \qquad R—CH_2—CH$$
$$\mid \qquad\qquad\qquad \parallel$$
$$:S: \quad \longleftrightarrow \quad :S \cdot$$
$$\mid \qquad\qquad\qquad \mid$$
$$COCH_3 \qquad\qquad COCH_3$$

This stabilization of the radical also explains our other experimental observations satisfactorily.

In radical polymerization, as is well known, the rate of polymerization depends on the concentration of the initiator to the power of 0·5; on the other hand, in the presence of inhibitors—substances giving stable radicals in radical processes—this magnitude approximates to unity [20]. Since in the polymerization of VTA the radicals of the thioesters are stabilized and inhibit their own polymerization, in essence one must speak of an autoinhibition effect. The stability of the radicals formed from the monomer also explains the relatively high activation energy [20].

The possibility of the formation of stable radicals also explains the high chain-transfer constant of AETA and its marked inhibiting action on the polymerization of VAc. Chain transfer by thioesters most probably proceeds in such a way that the attacking radical (R·) detaches a hydrogen atom from the carbon linked to the sulphur

$$R\cdot + \underset{\underset{\underset{COCH_3}{|}}{\underset{:S:}{|}}{CH_2} \underset{\underset{\underset{COCH_3}{|}}{\underset{O}{|}}}{CH_2} \qquad RH + \underset{\underset{\underset{COCH_3}{|}}{\underset{:S:}{|}}}{\cdot CH} \underset{\underset{\underset{COCH_3}{|}}{\underset{O}{|}}}{CH_2} \longleftrightarrow \underset{\underset{\underset{COCH_3}{|}}{\underset{:S\cdot}{\|}}}{CH} \underset{\underset{\underset{COCH_3}{|}}{\underset{O}{|}}}{CH_2}$$

*Investigations on the synthesis of poly-(vinyl mercaptan) and a copolymer of vinyl mercaptan and vinylamine.* Poly-(vinyl mercaptan) (PVM) can be obtained by the acid or alkaline saponification of PVTA [3–5]. One of the methods of obtaining polyvinylamine may be the conversion of a polyvinylimide by Gabriel's method. Thus, Reynolds and Kenyon [21] have synthesized polyvinylamine from polyvinylphthalimide by reaction with hydrazine hydrate with subsequent treatment of the resulting product with hydrochloric acid.

Taking into consideration the fact that low-molecular-weight thioesters can be converted into mercaptans [22] by means of hydroxylamine, hydrazine, and substituted hydrazines, it has been suggested that when the VTA–VSI and VTA–VPI copolymers were transformed by Reynolds and Kenyon's method [21], the imine group would be converted into an amino group and the thioester group into a mercapto group and the result would be the formation of the following copolymer:

$$-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_2-\underset{\underset{SH}{|}}{CH}-$$
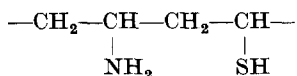
(the copolymer may of course contain small amounts of unchanged imide and thioester groups).

On investigating the saponification of PVTA, we obtained results analogous to those in the literature [3–5]. When PVTA was treated with a 10% solution of NaOH in methyl alcohol, saponification took place rapidly at 20°. When the solution was acidified, PVM precipitated (content of residual thioacetate groups ~10%). The softening point of the polymer was 64–66°. PVM does not

dissolve in organic solvents and is soluble only in a methanolic solution of NaOH at pH=8·5. The solution of PVM is sensitive to air and on standing in the air the PVM precipitates, apparently because of the oxidation of the —SH groups to disulphide groups with the formation of a three-dimensional lattice.

On reaction with hydrazine hydrate in air, the VTA—VSI and VTA—VPI copolymers gave insoluble highly swollen products. In the hydrazine hydrate reaction and on treating the mixture with hydrochloric acid, a strong smell of hydrogen sulphide was detected. The processes of cross-linking and evolution of hydrogen sulphide could not be prevented even when the reaction was carried out in nitrogen. The nitrogen that had been bubbled through the reaction mixture was passed through a solution of cadmium acetate to determine the amount of hydrogen sulphide evolved by the iodometric method. In this way, ∼10% of the sulphur split off from the polymer was trapped in the form of cadmium sulphide.

## CONCLUSIONS

The kinetics of the polymerization of vinyl thioacetate is characterized by an extremely high rate of chain transfer by the mononer molecule ($C_M$=0·056 at 60°), as a result of which resonance-stabilized radicals are formed (through $d$–$\pi$ conjugation). This is confirmed by the fact that the chain-transfer constant of 2-acetoxyethyl thioacetate in the polymerization of vinyl acete ($C_S$=0·0132 at 60°) has the same order of magnitude as the chain-transfer constant of monomeric vinyl thioacetate; under these conditions, 2-acetoxyethyl thioacetate has an inhibiting action on the polymerization process. From the copolymerization constant of vinyl thioacetate (with N-vinylsuccinimide, N-vinylphthalimide, and N-vinylcarbazole) have been determined the magnitudes of $Q$ (1·67) and $e$ (−1·34), these values being considerably higher than the corresponding ones for vinyl acetate. From these results it may be concluded that the replacement of an oxygen atom by a sulphur atom increases the reactivity of the monomer (as a result of $d$–$\pi$ conjugation) and the electronegativity of the radical formed, this being due to the strong electron-donating nature of sulphur. By treating the copolymers (vinyl thioacetate–vinylsuccinimide and vinyl thioacetate-vinylphthalimide) with hydrazine hydrate it was possible to obtain polymers containing free—SH and—NH₂ groups, which rapidly oxidized in the air.

*Translated by* B. J. HAZZARD

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