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POLYSULPHIDE LINKAGES IN POLYPROPYLENE SULPHIDE PREPARED USING ZINC AND CADMIUM THIOLATE INITIATORS

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Abstract—In the polymerization of propylene sulphide using zinc thiolate initiators, substantial amounts of propylene are produced. This reaction is accompanied by the incorporation of sulphur as di- or polysulphide linkages in the polymer chain. Up to 15 per cent of the monomer has been found to participate in this side reaction and up to one in ten of the linkages to be polysulphidic. No elemental sulphur is formed. The polymers are cleaved by *n*-butane thiol/piperidine and by tri *n*-butyl phosphine/water to give low mol. wt. thiol terminated products. Substantial amounts of sulphur can be removed by treatment with triphenyl phosphine.

Polymerization using cadmium thiolates was accompanied by very small amounts of propylene, difficult to distinguish from that present in monomer as an impurity. The polymers produced with these catalysts are essentially monosulphide but probably contain a small proportion of polysulphide linkages.

INTRODUCTION

POLYPROPYLENE sulphide is an elastomer with mechanical properties similar to those of the polysulphide elastomers.(1) The high compression set and rapid stress relaxation of crosslinked propylene sulphide copolymers are higher than would have been anticipated for a polymer containing monosulphide main chain linkages; the suggestion has been made that the products contain polysulphide structures.(2)

This paper brings evidence to show that certain polypropylene sulphides do contain substantial proportions of polysulphide linkages.

EXPERIMENTAL

Propylene liberation

The initiators were dissolved in propylene sulphide in crown-capped bottles; polymerization was allowed to go to completion over periods up to 1 week at room temperature or 50°. The atmosphere above the solid polymer was sampled by hypodermic syringe and analysed for propylene by gas chromatography. From this analysis and the total volume, the amount of propylene was estimated. The results in Table 1 are semiquantitative since a small amount of propylene remained dissolved in the solid polymer. However, sulphur contents of isolated polymers were within 0·1 per cent of those calculated from the amount of propylene liberated.

Reactions of polypropylene sulphide

(*a*) *With* n-*butane thiol/piperidine*

Polymer zinc [bis(allyl thiolate) 5×10^{-3} mole/l. polymerization temperature 20°; S 46·7 per cent] (5g), in piperidine (25g) and *n*-butane thiol (10g) for 4 days at room temperature. The mixture was acidified with excess dilute HCl and extracted with ether. The ether layer, after removal of solvent and excess butane thiol, gave di-*n*-butyl disulphide (1·5g) and a liquid polymer (4·4g) (SH content 6·8 per cent).

(*b*) *With triphenyl phosphine* (*TPP*)

(*i*) Polymer [preparation as in (*a*); S 46·7] (4g) heated with TPP (2g) at 100° for 20 hr. The product was extracted repeatedly with 65/35 methanol/water to give polymer (3·16g; S 44·17 per cent) and crude TPPS (2·27g). Recrystallization of the latter gave pure TPPS (1·60g) and a residue from which low mol. wt. polymer (0·42g) was isolated.

(*ii*) As (*i*) except that polymer (0·25g) and TPP (1g) were used. Removal of unchanged TPP and TPPS by repeated extraction with light petroleum left residual polymer (0·15g).

Integral TGA measurements (heating rates 3°/min) were carried out on the original polymer and on treated polymer (*i*). The onset of decomposition for both polymers was at 210° and temperatures for maximum rates of decomposition were at 250° and 260° respectively.

(*iii*) Polymer [cadmium bis(allyl thiolate) 7 × 10^{-5} mole/l.; S 42·5 per cent] (4g) heated with TPP (0·25g) as in (*i*).

(*c*) *With tri* iso*propyl phosphite* (*TIPP*)

(*i*) Polymer *b*(*i*) (4g) was treated with TIPP (2g) for 16 hr 100°. Rapid reduction in viscosity occurred and the initially two-phase mixture became homogeneous and fluid. After 18 hr at 100°, the mixture was cooled and excess TIPP removed by extraction with ethanol. The residue (A)(2·85g) after removal of solvent was a semi-liquid polymer (SH content 0·40 per cent). The alcohol extracts were concentrated and after shaking with 5 N HCl a liquid polymer (B) with a strong thiol-like odour (1·15g) was isolated.

(*ii*) As (*i*) but the reaction mixture dissolved in ether/benzene and washed with cold concentrated HCl. Isolated polymer contained 0·19 per cent SH.

(*iii*) Polymer *b*(*iii*) (2g) and TIPP (0·125g) were reacted at 100° for 16 hr.

(*d*) *With tri* n-*butyl phosphine* (*TBP*)/*water*

Polymers (*b*)(*i*) (2g) and (*b*)(*iii*) (2g) each in benzene (25 ml) and ether (10 ml). To (*b*)(*i*) was added TBP (1 ml) in ethanol (5 ml) + water (1 ml) and to (*b*)(*iii*) TBP (0·3 ml) in ethanol (2 ml) + water (0·25 ml)

Reactions were carried out in crown-capped bottles under N_2 for 16 hr at room temperature followed by 6 hr at 50°.

Solvents were removed to leave degraded polymers containing unchanged TBP and the products (oxide and sulphide) from the reactions with polymers. The SH content of treated but unpurified (*b*)(*i*) was 4·9 per cent and, after correcting for the low mol wt. phosporus compounds present (P= 5·19 per cent), this corresponds to a thiol content of the polymer of 7·8 per cent.

Molecular weights of polymers

Molecular weights were obtained by GPC using the Waters Associates instrument. Tetrahydrofuran was the solvent. Calibration was performed with fractions of high mol. wt. polypropylene sulphide using $\bar{M}_w$ obtained from light scattering measurements. Chromatograms and integral distributions curves are given in Figs. 1 and 2, and averages for the various poymers in Table 2. The low mol. wt. phosphorus compounds (TPP, TIPP, etc.) were resolved quite distinctly from the polymers and were ignored in the GPC traces shown and in calculation of mol. wt. data. For this reason and because of changes from experiment to experiment in the sensitivity range of the instrument detector, the curves in Figs. 1 and 2 are not equal in area.

Element analysis and thiol contents of polymers

Sulphur was determined by the oxygen bomb method followed, after oxidation by H_2O_2, by titration with barium perchlorate in the presence of "thorin" indicator. Thiol content was determined by dissolving the polymer in pyridine—$AgNO_3$ and titrating the liberated nitric acid.

RESULTS AND DISCUSSION

In the polymerization of propylene sulphide by zinc thiolates(3) propylene is formed in large amounts but there is no clearcut relationship with the amount of initiator or with the temperature of polymerization (Table 1). Low concentrations of zinc thiolates, which result in slow polymerization, gave the highest yields, up to 15 per cent (based on monomer) of propylene. It has been found that propylene is only formed concurrently with polymerization; the polymer itself is quite stable under the reaction conditions employed but when propylene sulphide is added to a polymer containing active initiating centres (the polymerization has been shown to be non-terminating(3)) polymerization occurs with liberation of more propylene.

TABLE 1. LIBERATION OF PROPYLENE DURING THE POLYMERIZATION OF PROPYLENE SULPHIDE

Concentration (mole/l. × 10^2)	% Propylene	[η] polymer	% S	$\bar{M}_w$	$\bar{M}_n$
				× 10^{-3}	
(i) Zinc bis(allyl thiolate)					
0·5	12·5	0·42	46·40 46·72		—
0·5*	15·0	—	46·71	17·3	1·56
1·0	3·4	—	—	—	—
2·5	7·3	0·39	45·00	25·1	2·53
5·0	4·1	—	—		—
10·0	4·5	0·23	43·36		—
(ii) Cadmium bis(allyl thiolate)					
0·1	0·3†	0·75	—		—
0·2	0·2(5)	—	—		—
0·5	0·3	0·62	43·39	66·2	25·7
1·0	0·4	—	—		—
2·5	0·5	0·44	43·13	43·1	14·5

* 50°C.

† Individual values in this group are not very precise and sample-to-sample variation is not significant because of the small but variable contribution (0·1–0·15 per cent) from propylene in the monomer, which could not be removed.

The amount of propylene from cadmium thiolate initiated polymerization is very much smaller. The amounts varied from 0·18 to 0·47 per cent w/w on the monomer using from 1 to 25 × 10^{-3} mole/l. of catalyst at temperatures between 20° and 50°. However, propylene is a persistent impurity in propylene sulphide freed from mercaptans by treatment with lead oxide. Thus in monomer purified this way followed by distillation and outgassing with nitrogen, propylene contents of 0·09 to 0·15 per cent w/w were determined. There was also a possibility of traces of propylene arising from adventitious sources; for example, self-sealing elastomer gaskets (which contain zinc compounds as vulcanization accelerators) can give rise to propylene formation. However, as the amounts obtained were greater than that present as an impurity, it is considered that a small amount is produced. The polymers of all types were homogeneous and transparent, and contained no free sulphur, since a hot solution of the polymer with bright copper or silver gauze gave no metal sulphide. The sulphur contents of zinc catalyzed polymers were in good agreement with calculation from the amount of propylene formed during polymerization. Molecular weight distributions of polymers in which propylene is produced in significant quantities are extremely broad and in marked contrast with those in which there is little or no side reaction. Thus, with cadmium thiolate initiators $\bar{M}_w/\bar{M}_n$ has been found to be in the range from 2·5 to 3·7 whereas some of the zinc thiolate initiated polymers have values of $\bar{M}_w/\bar{M}_n$ between 10 and 15, and inspection of the distributions (e.g., Fig. 1 curve C) shows the presence of a large amount (~ 10 per cent) of very low mol. wt. species. At higher initiator concentration when a small amount of propylene is produced, a narrower distribution of mol. wts. is found (Fig. 1 curve D). The corresponding distributions for the cadmium thiolate initiated polymers (Fig. 1 curves A and B) are more normal and, for a given initiator concentration, are higher in mol. wt. It seems reasonable, therefore, to associate the effects on mol. wt. and mol. wt. distribution with the sulphur incorporation reaction.

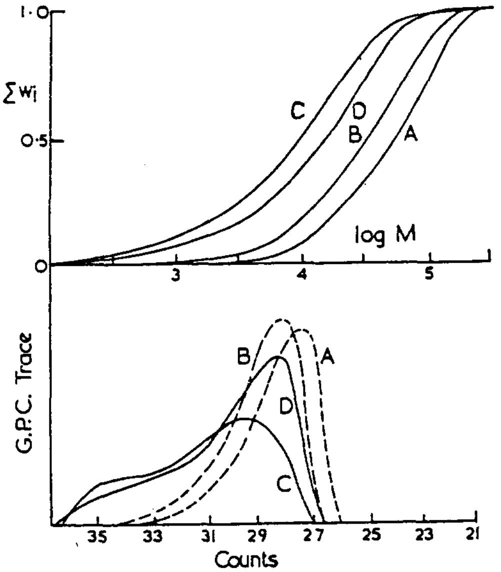

Fig. 1. Molecular weight distributions of polypropylene sulphides

Curve	Initiator M $(SCH_2CH{=}CH_2)_2$	Conc. (mole/l × 10^2)
A	M = Cd	0·5
B	Cd	2·5
C	Zn	0·5
D	Zn	2·5

As there is no free sulphur present, the extra sulphur must be as di- or polysulphide linkages, and several characteristic reactions were used to confirm this.

The first of these was cleavage by a large excess of a primary thiol/piperidine mixture,$^{(4)}$ the reaction of which can be idealized in Eqn. (1):—

$$-R-S_x- + 2(x-1)R'S^-X^+ \longrightarrow R(S^-X^+)_2 + (x-1)\,R'_2S_2 + (x-2)S^{=}(X^+)_2 \qquad (1)$$

where

$$R = (SCHMeCH_2-)_n \quad R' = \text{Alkyl}; \quad X = C_5H_{10}NH_2.$$

When treated with excess *n*-butane thiol/piperidine, a zinc bis(allyl thiolate) catalyzed polypropylene sulphide containing 46·71 per cent sulphur (the sulphur content calculated for polypropylene monosulphide is 43·24 per cent) gave a liquid low mol. wt. polymer with thiol end groups, and 90 per cent of the theoretical yield of di *n*-butyl disulphide based on the excess sulphur content.

In another experiment the polymer was reacted with triphenyl phosphine (TPP) (in excess of that required to react with the sulphur which could be present as polysulphide). It was found that 74 per cent of the excess sulphur was removed from the polymer by TPP at 100°, with the isolation of the corresponding amount of triphenylphosphine sulphide (TPPS).

This would indicate that most of the sulphur is present as polysulphides since alkyl disulphides, unlike alkenyl disulphides, are unreactive to TPP.(5, 6) However, from the mol. wt. of the cleaved polymer and the excess sulphur content, the polysulphide linkages cannot on average contain more than 2 or 3 sulphur atoms. Hence, as most of the sulphur is removed by TPP, it would appear that a proportion of the disulphides have been converted to monosulphides. It could well be that the attachment of two sulphide or polysulphide linkages to each propylene unit could increase the ease of desulphuration but, without experiments on suitable model compounds, this is no more than a speculative explanation for the observations. Another anomaly in the results of the TPP treatment concerns the mol. wt. of the treated polymer. Desulphuration should result in no great fall in mol. wt. which is contrary to experiment. (Fig. 2 curve A and Table 2).

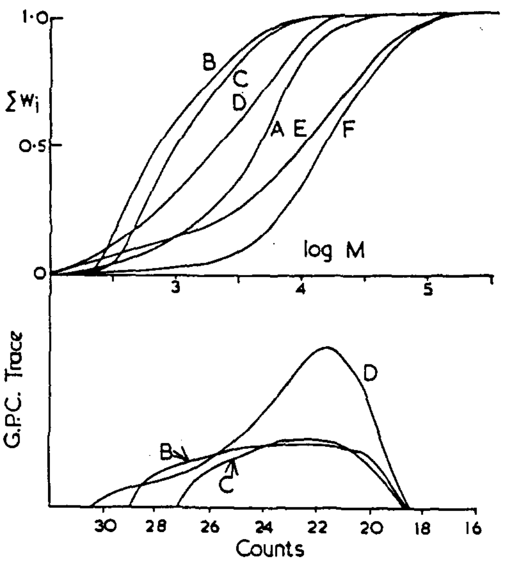

FIG. 2. MOLECULAR WEIGHT DISTRIBUTIONS OF TREATED ZINC BIS(ALLYL THIOLATE) INITIATED POLYPROPYLENE SULPHIDES

Curve	Treatment	
A	TPP[a]	a high MW columns
B	n-BuSH/$C_5H_{10}NH$[b] (a)	b low MW columns
C	TBP/H_2O[b] (b)(i)	
D	TIPP[b] (c)(ii)	
E[c]	Untreated (for A, C, D)[a]	
F[c]	Untreated (for B)[a]	

c = Preparative conditions identical except for polymerization temperature E 20°, F 50°.

TABLE 2. MOLECULAR WEIGHTS OF POLYPROPYLENE SULPHIDES

Treatment	Expt.	Polymer	$\bar{M}_w$		$\bar{M}_n$	
			Initial	Treated	Initial	Treated
(i) Zinc bis(allyl) thiolate						
n-BuSH/$C_5H_{10}NH$	(a)		22700	1560	2200	630 500*
TPP	(b)	(i)	21100	7000	1460	1880†
		(ii)	21100	7100	1460	790‡
TIPP	(c)	(i)A	21100	4430	1460	1800
		B	21100	1270	1460	428
		(ii)	21100	3890	1460	1250
TBP/H_2O	(d)		21100	1900	1460	190

(ii) Cadmium bis(allyl thiolate) $\bar{M}_w$ (Initial) 94000
$\bar{M}_n$ (Initial) 35000

Treatment			After treatment	
			$\bar{M}_w$	$\bar{M}_n$
TPP	(b)	(iii)	55400	22000
TIPP	(c)	(iii)	77600	25800
TBP/H_2O	(d)		26700	9600

* Vapour pressure osmometry.

† Low mol. wt. fraction lost during isolation.

‡ High resolution columns showed presence of a fraction (~ 40 per cent of total) with $\bar{M}_w$ = 8700 and $\bar{M}_n$ = 6900 in this polymer.

A possible explanation for this fall is that some of the disulphide linkages have been reduced to thiols by TPP resulting from the presence of water. This reaction is known to occur,(7) and is supported by the observation that the polymer isolated after extraction of excess TPP and TPPS (with aqueous alcohol) contained 0·6 per cent w/w of thiol groups, compared with a negligible amount in the initial polymer.* However, this would not explain why a comparable fall in mol. wt. occurred even when no water was present in the reaction, other than as adventitious traces.

Two other phosphorus-containing reagents which *are* known to cleave aliphatic disulphides were examined for comparison with TPP. These are alkyl phosphites,(8) and alkyl phosphines in the presence of water.(9)

Their reactions with polypropylene polysulphide would be as indicated in Eqns. (2) and (3)

$$-R-S_x- + (x-1)\,R_3'P + H_2O \longrightarrow R(SH)_2 + (x-2)R_3'PS + R_3'PO \qquad (2)$$

$$-R-S_x- + (x-1)\,(R'O)_3P \longrightarrow R'SRSP(O)\,(OR')_2 + (x-2)\,(RO)_3'PS \qquad (3)$$

Tri n-butylphosphine (TBP) in the presence of water gave a liquid product with thiol end groups, with, as would be expected from the reaction mechanisms, mol. wt. and molecular distribution almost identical with those for the polymer obtained using the

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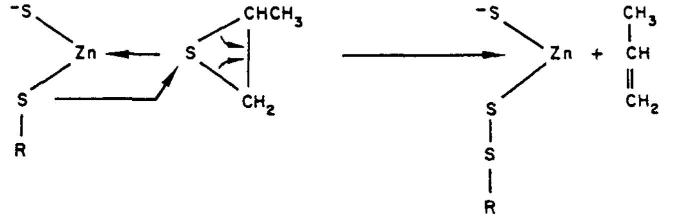
* The terminal unit in the polymer chain would be attached to zinc and therefore would not react in the analytical determination.

n-butane thiol/piperidine reagent (Fig. 2) (curves B and C). Tri *iso*-propylphosphite (TIPP) also greatly reduced the mol. wt. of the polymer (Fig. 2 curve D) and in conformity with Eqn. (3), the degraded polymer had negligible thiol functionality. (The small amount determined probably arose from some hydrolysis of the thiophosphate ester groups during isolation.)

The more extensive degradation brought about by these reagents compared with TPP is apparent from the mol. wt. averages, and in these cases there seems little doubt that most or all of the poly and disulphide linkages in the polymer have been cleaved.

The formation of polysulphides is most likely as a side reaction in the insertion step in the zinc thiolate propagated polymerization (Eqn. 4),



(4)

while the low mol. wts. observed when propylene formation is a major side reaction must be the result of a transfer reaction. This could arise from the instability of the zinc polysulphides which would be expected to eliminate zinc sulphide (this would then re-initiate polymerization) with the formation of a non-propagating polysulphide. (Eqn. 5)

$$P_a{-}S_x{-}Zn{-}S{-}P_b \rightarrow P_a{-}S_x{-}P_b + ZnS. \qquad (5)$$

This reaction would be competitive with the propagation reaction. The latter is favoured as shown by the presence of much polymer of high mol. wt. but containing a large number of polysulphide linkages. (The peak mol. wt. is reduced from ~ 20,000 to ~ 1000 on reductive cleavage.)

Polymer treated with TPP is marginally more stable thermally than the original. This could be due either to removal of polysulphidic sulphur or of catalyst residues, both of which could act as sites for the initiation of degradative reactions.

It has been reported previously(3) that thiols reduce the mol. wt. of polypropylene sulphide in proportion to their concentrations, and this was ascribed to the transfer reaction (Eqn. 6).

$$-Zn{-}S{-}P_a + RSH \rightarrow ZnSR + P_aSH. \qquad (6)$$

The existence of polysulphide linkages in the chain raises the possibility also of a transfer reaction as indicated in Eqn. (7).

$$-P_a{-}S_x{-}P_b{-} + RSH\,(\text{or } RSZn{-}) \rightarrow -P_aSH\,(\text{or } P_a{-}SZn{-}) + RS_x{-}P_b{-} \qquad (7)$$

However, thiols reduce the mol. wt. irrespective of whether or not significant amounts of propylene are liberated and therefore, although this type of reaction cannot be excluded, it cannot be important.

The structure of the cadmium thiolate initiated polymers is much less certain. Although the propylene found during the polymerization was always greater than that present in the monomer as impurity, its small and variable amount make it unwise to rely on this observation alone for the presumption of di- or polysulphide linkages in these polymers; some more sensitive test was required. The sulphur contents of cadmium thiolate initiated polymers are (within experimental error) the same as calculated for polypropylene monosulphide. Neither i.r. nor u.v. spectroscopy have been found definitive for polysulphide linkages and spectra of both zinc and cadmium initiated polymers were very similar. The former did show a greater absorption in the 260–280 nm region, which may well result from the polysulphide linkages, while the latter possessed only a small shoulder at 230 nm.

Stress relaxation on crosslinked polymers would provide a measure of any degradation occurring; it should be possible, in principle, to distinguish between scission involving the polymer chain and that at crosslinkages. In view of the possible modification of polymer structure, other than by crosslinking, by vulcanizing agents (peroxides degrade the polymer and sulphur itself appears to undergo some reaction) this approach was not tried. Instead, the influence on the mol. wt. of the polymer of reagents which desulphurize or cleave polysulphide chains was studied. The effects of TPP, TIPP and TBP/H_2O on a high mol. wt., cadmium *bis*(allyl thiolate) initiated polymer are given in Table 2. It is seen that there is a fall in mol. wt. in all cases, but it is not very great. The TBP/H_2O reagent had the greatest effect, but even if this were wholly ascribed to scission of polysulphide linkages there can be very few of them—less than one per hundred monomer units at the most. This estimate, however, which is clearly approximate and tentative, is of the same order as that calculated from propylene liberation.

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Résumé—Au cours de la polymérisation du sulfure de propylène, amorcée par des thiolates de zinc, il se forme une quantité non négligeable de propylène. Cette réaction coincide avec l'incorporation de soufre dans la chaîne polymérique sous forme d'enchaînements di ou polysulfure. On a trouvé que jusqu'à 15 pour cent du monomère participe à cette réaction secondaire et que jusqu'à 10 pour cent des enchaînements ainsi produits sont des polysulfures. Il n'y a pas formation de soufre élémentaire. Les polymères sont coupés par des mélanges de *n*-butane thiol avec la pipéridine et de phosphure de tri *n*-butyle avec l'eau pour donner des produits de faible masse moléculaire terminés par des groupements thiol. D'importantes quantités de soufre peuvent être enlevées par traitement avec le phosphure de tri-phényle.

A l'issue de la polymérisation utilisant des thiolates de cadmium on trouve de très faibles quantités de propylène, difficiles à distinguer de celui présent dans le monomère comme impureté. Les polymères produits au moyen de ces catalyseurs comportent essentiellement des enchaînements monosulfure ainsi que, probablement, une faible proportion de polysulfure.

Sommario—Nella polimerizzazione del solfuro di propilene usando iniziatori di tiolato di zinco viene prodotta una notevole quantità di propiline. Questa reazione è accompagnata dall'incorporamento di solfuro come legami di di- o polisolfuro nella catena polimerica. Si è trovato che più del 15% del monomero partecipa in questa reazione collaterale e più di uno su dieci dei legami è polisulfidico. Non si forma zolfo. I polimera sono sfaldati da *n*-butano-tiolo/piperidina e da tri-*n*-butil fosfinato/acqua per dare prodotti terminali a basso peso molecolare di tiolo. Notevoli quantità di zolfo possono essere estratte con il trattamento con trifenil-fosfina.

La polimerizzazione usando tiolati di cadmio era accompagnata da piccolissime quantità di propilene, difficili da distinguere da quella presente nel monomero come impurità.

Zusammenfassung—Bei der Polymerisation von Propylensulfid mit Zinkthiolat-Initiatoren werden erhebliche Mengen an Propylen gebildet. Diese Reaktion wird begleitet von einem Einbau von Schwefel als Di- oder Polysulfidbindung in die Polymerkette. Es wurde gefunden, daß bis zu 15 Prozent des Monomeren an dieser Nebenreaktion beteiligt sind und bis zu ein Zehntel der Bindungen als polysulfidische Bindugen vorliegen. Elementarer Schwefel wird nicht gebildet. Die Polymeren werden durch *n*-Butanthiol/Piperidin und durch Tri-*n*-butylphosphin/Wasser gesplaten zu niedermolekularen Produkten mit endständigen Thiolgruppen. Auch kann durch Behandlung mit Triphenylphosphin ein wesentlicher Teil des Schwefels entfernt werden.

Die Polymerisation unter Verwendung von Cadmiumthiolaten führt zur Bildung sehr geringer Mengen an Propylen, die sich nur schwieirg von dem als Verunreinigung im Monomeren vorliegenden unterscheiden lassen. Die mit diesen Katalysatoren erhaltenen Polymeren sind überwiegend monosulfidisch gebunden, enthalten aber vermutlich einen geringen Anteil polysulfidischer Bindungen.