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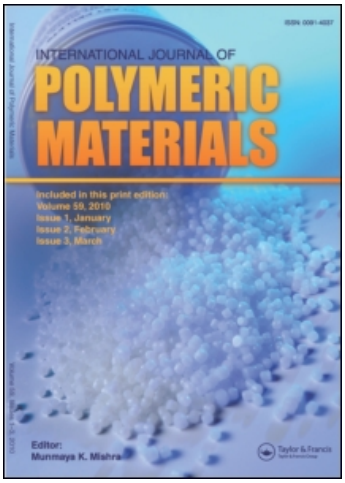

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Curing of Poly-(1,4-Phenylene Sulphide) in the Presence of its Oligomers

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The curing of poly-(1,4-phenylene sulphide) with its HS-terminated oligomers has been studied. The influence of crosslinking on crystallinity of poly-(1,4-phenylene sulphide) has been examined. The mechanism of curing has been discussed.

Keywords: Poly-(1,4-phenylene sulphide); Poly-(1,4-arylene sulphide); Curing

INTRODUCTION

Poly-(1,4-phenylene sulphide) (PPS) is an important high-performance polymer, possesing good chemical resistance and thermal stability.

It is insoluble in all solvents at room temperature. PPS is often used as a protective coating to increase the chemical resistance of the base material.

The most important characteristic of pps is its ability to undergo change upon heating. The change is complex in nature and is not fully explained. Extensive literature exists on reactions in pps during heating [1–5]. These reactions (oxidation, crosslinking, chain extension) will be referred as "curing" in this text. The role of thiol groups in pps curing was studied by Port and Still [5]. The

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participation of the thiol groups was concerned in our earlier research [6].

The purpose of our recent work was to determine thiol-terminated pps oligomers influence on the curing process of high molecular pps. The application of such additive guarranties crosslinking links of pps-like structure.

EXPERIMENTAL

The polymer was commercial material Ryton P-3 from Phillips Petroleum Company. PPS was prepared before experiments as in our previous work [6].

As additives two kinds of pps oligomers with HS-terminated chains were used:

Oligomer A has molecular weight 870 and oligomer B has molecular weight 1180.

Oligomers were obtained and characterized according to the procedure described by Yang [7]. The reaction occurs in two steps: I-polycondensation of disodium sulphide and 1,4-dichlorobenzene-molar ratio 1/1; II-termination of the chains of obtained oligomers with HS-groups.

The samples of pps mixed with oligomers were cured in argon atmosphere, at temperature 295 ± 5°C.

Elemental analysis was carried out using a Perkin – Elmer automatic analyser. Crystallinity was measured from X-ray diffraction-patterns which were obtained using TUR M-62 diffractometer with Cu K_α radiation. Crystallinity degree was determined according to Brady's method [8].

RESULTS

The composition of cured samples in shown in Table I.

The results of curing pps with its oligomers are shown in Tables III and IV.

Crystallinity degree of pps heated for 20 min. in argon atmosphere is 70%.

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TABLE I Composition of cured samples

	Sample characterisation		
Sample	*Oligomer* [%]	*pps* [%]	*Curing time* [*min.*]
A_{10-20}	A10	90	20
A_{10-40}	A10	90	40
A_{10-60}	A10	90	60
A_{20-20}	A20	80	20
A_{20-40}	A20	80	40
A_{20-60}	A20	80	60
A_{30-20}	A30	70	20
A_{30-40}	A30	70	40
A_{30-60}	A30	70	60
B_{10-20}	B10	90	20
B_{10-40}	B10	90	40
B_{10-60}	B10	90	60
B_{20-20}	B20	80	20
B_{20-40}	B20	80	40
B_{20-60}	B20	80	60
B_{30-20}	B30	70	20
B_{30-40}	B30	70	40
B_{30-60}	B30	70	60

TABLE II Characteristic of pps oligomers

	Molecular	*Elemental composition*, [%]				*Flow*	*Content of*	*Content of Cl*
Sample	*weight*[1]*	*C*	*H*	*S*	*Cl*	*temperature* [°*C*]	*HS-terminated chains [%]*	*containing chains* [%]
A	866	65,91	3,87	29,01	0,87	281–284	73,8	26,2
B	1176	65,82	3,98	29,02	0,65	282–285	88,6	11,4

*By DP calculation according to Rajan and coworkers [9].

TABLE III Elemental composition of cured pps

	Content [%]			
Sample	*C*	*H*	*S*	*Cl*
pps without admixture	66,28	3,50	28,34	0,79
A_{30-60}	65,05	3,50	28,85	0,81
B_{30-60}	66,10	3,54	28,68	0,75

DISCUSSION

According to Port and Still [5] thiophenyl radicals take part in the curing of pps. Under the curing conditions thiophenyl radicals could

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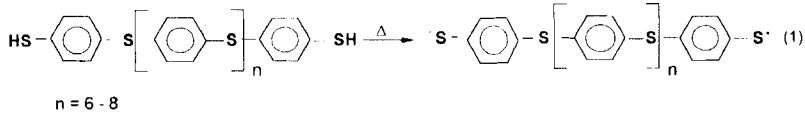
TABLE IV Crystallinity of pps cured with its oligomers

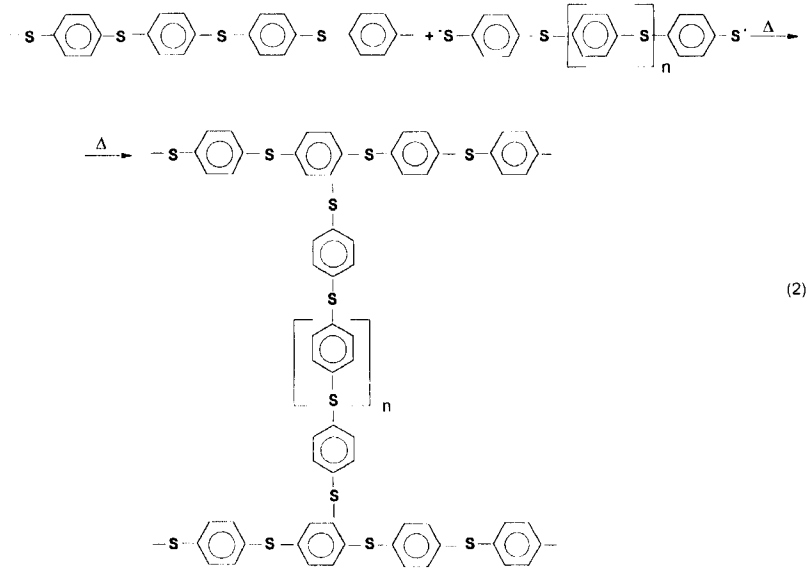
Sample	*Crystallinity degree* [%]	*Sample*	*Crystallinity degree* [%]	*Sample*	*Crystallinity degree* [%]
$A_{10\text{-}20}$	50,7	$A_{20\text{-}20}$	51,0	$A_{30\text{-}20}$	48,4
$A_{10\text{-}40}$	49,2	$A_{20\text{-}40}$	48,8	$A_{30\text{-}40}$	46,4
$A_{10\text{-}60}$	50,5	$A_{20\text{-}60}$	47,4	$A_{30\text{-}60}$	44,6
$B_{10\text{-}20}$	51,7	$B_{20\text{-}20}$	50,8	$B_{30\text{-}20}$	46,6
$B_{10\text{-}40}$	48,0	$B_{20\text{-}40}$	47,3	$B_{30\text{-}40}$	47,9
$B_{10\text{-}60}$	47,1	$B_{20\text{-}60}$	48,3	$B_{30\text{-}60}$	47,0

be created as a result of decomposition of HS-groups (1) or S—S bonds, which could be formed in the polymer by oxidation during the polymer preparation.



n = 6 - 8

PPS oligomers with HS-terminated chains are potentially good curing agents for high molecular pps because of the presence of active groups and identity of formed crosslinking chains structure with structure of pps (2).



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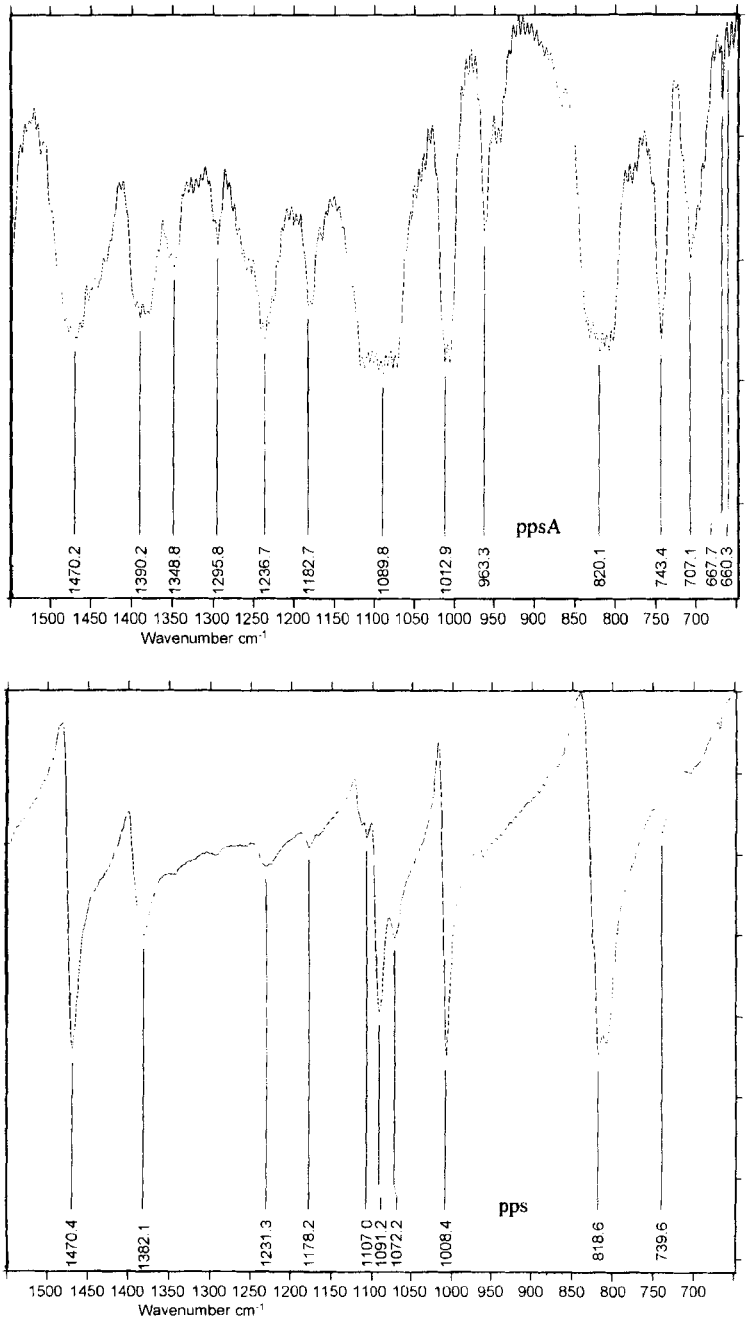

FIGURE 1 Ft-IR spectra (KBr) of pps without additives (pps) and pps containing 30% oligomer A (pps A).

The influence of oligomers amount and heating time on curing was studied by determination of crystallinity degree. According to Brady [8] pps curing decreases its crystallinity.

Both oligomers (A and B) decrease crystallinity (Tab. IV) degree of pps. This fact allow us to suggest that they take part in curing reactions.

In the case of oligomer A the decrease of crystallinity degree increases with increase of additive amount and with increase of heating time (Tab. IV).

Similar dependence we observed in the case of oligomer B (Tab. IV). We practically didn't observe a significant difference of crystallinity degree of cured polymers, however the lowest value of crystallinity degree (44%) is for pps cured with 30% oligomer A during heating for 60 minutes while crystallinity of pure pps is 70%.

IR spectrum could not be recorded for samples cured with oligomer B admixture because the samples could not be pulverised.

FT-IR spectrum (Fig. 1) was recorded for sample of pps with 30% of oligomer A, heated for 60 minutes. Additional absorption at ca. $870\,cm^{-1}$ due to trisubstituted benzene ring was observed which suggests that curing results in branching and crosslinking.

The comparison (Tab. III) of elemental analysis results of pps cured with additives and pps cured without admixture do not revealed significant differences.

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CONCLUSIONS

HS-terminated pps oligomers are effective curing agent for high molecular pps. Their effectiveness is practically independent on molecular weight, in the range 870 – 1180.

Acknowledgement

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