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Synthesis of oxidation stabilized cyclopentadiene polymers via cationic copolymerization with 4-isopropenylphenol

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Summary

A method is described to improve the oxidation stability of cyclopentadiene co- and terpolymers via cationic polymerization using 4-isopropenylphenols as polymerizable comonomers. The efficiency of these phenols depends on their part in the copolymer and on the number and size of their alkyl groups.

Introduction

In order to avoid or to retard the oxidative degradation of polymers, especially of polydienes, by reaction with oxygen, the addition of antioxidants is often necessary. Tertiary aromatic amines and sterically hindered phenols, for example 2,6-di-t-butyl-p-cresole are used for this purpose. As low molecular antioxidants can be exuded especially during the processing of the polymers, high-molecular-weight nonfugitive, nonleachable stabilizers are used in an increasing measure. Another possibility is the chemical fixation of the antioxidants on the polymer which should be stabilized.

In principle, there exist two possibilities for the incorporation of oxidation stabilizers into the polymeric matrix. On the one hand, the oxidation stabilizer can be incorporated into the polymer by means of a polymer-analogous reaction. Examples for such a kind of reactions are the addition of 3-(4-hydroxy-3.5-di-t-butyl-phenyl)propanol on partially epoxidized polyisoprene (1) and the addition via carbene insertion onto polypropylene of 4-oxo-3.5-di-t-butyl-2.5-cyclohexadienylidene followed by dehydrogenation (2).

On the other hand, the incorporation can take place by copolymerization of the monomer and the polymerizable antioxidant. Examples for this type are the copolymerization of N-(4-hydroxy-3.5-di-t-butyl phenyl) methacrylamide with styrene and butadiene (3) and the emulsion polymerization of 2.6-di-t-butyl-4-isopropenyl (or vinyl) phenol with butadiene and isoprene (4). The radical polymerization in solution of these compounds with styrene, methyl methacrylate and n-butylacrylate is another example (5).

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This paper deals with the copolymerization of cyclopentadiene (CPD), whose homopolymer synthesized via cationic polymerization has no industrial importance because of its very high oxidation instability, with diverse 4-isopropenylphenols. The oxidation behaviour of the resulting polymers is also investigated.

Experimental

Materials

Dicyclopentadiene (DCPD; Merck) was dried using molecular sieves and fractionated twice over CaH_2. Then, the DCPD was thermally monomerized and the resulting cyclopentadiene (CPD) distilled using a Vigreux column, followed by a further distillation. The purified CPD was stored at -78 °C and freshly distilled (b.p. -41 °C) before use. Isobutene (IB, b.p. = -6 °C) was purified and dried in a steel flask by means of Na/K alloy.

The synthesis of 4-isopropenylphenol (m.p. 79 °C), 2-methyl-4-isopropenylphenol (m.p. 43 °C), 2-t-butyl-4-isopropenylphenol (m.p. 76 °C) took place according to (6) by alkaline decomposition of the corresponding bisphenols. These compounds are instable and polymerize spontaneously. Thus, they were used immediately after recrystallization from hexane/benzene, hexane and methanol (6), respectively, and drying (12 h, 3 Torr). Dichloromethane and toluene were purified accordimg to the common methods (7), followed by refluxing in a closed circulation distillation apparatus under argon for at least 12 h. The LEWIS acids $SnCl_4$, $TiCl_4$, $BF_3 \cdot OEt_2$ and $Et_3Al_2Cl_3$ were purified by fractional distillation in vacuum.

Polymerization

The polymerizations were carried out under inert conditions in heat-treated polymerization vessels which were directly connected with the circulation still. The solvents and the monomers were put into the reaction vessel; isobutene was condensed from a gratuated vessel. It is to be mentioned that 4-isopropenylphenol and 2-methyl-4-isopropenylphenol are not completely soluble in the solvents used.

After tempering the initiation was carried out by addition of the initiator by means of medical syringes to the vigorously stirred polymerization solution in an argon counter flow. After the reaction time wished the polymerizations were stopped by addition of some milliliters of a mixture of methanol and aqueous ammonia. The initiator residues were removed by means of filtration and the polymers precipitated in methanol (fivefold volume in respect of the polymerization solution). The copolymers were purified by a second precipitation from CH_2Cl_2/methanol and dried in vacuum. Deviating therefrom, the copolymers used for the investigation of the oxidation behaviour were freed from residual phenolic monomers, which act as stabilizers, by a fourfold precipitation.

Measurements

The number average molecular weights $\bar{M}_n$ were determined by a KNAUER vapour pressure osmometer in benzene at 45 °C.
^{1}H-NMR-spectra were recorded using the KRH 100 R 100 MHZ-spectrometer of the Centre for Construction of Scientific Instruments of the Academy of Sciences of the GDR.
CDCl$_3$ and dioxane-d$_8$ were used as solvents and HMDS and benzene, respectively, as internal standards. The quantitative evaluation of the spectra was made by repeated planimetration. IR spectra were recorded on a VEB Carl Zeiss Jena UR 20 spectrometer using KBr pressing practice.

Results and Discussion

As investigations by RUSSEL, BAUER and VAIL (8-11) show on the example of IB polymerization, phenols take part in the polymerization process in a very complex manner. They can act as coinitiators, transfer and termination agents. These properties are said to be the reason that cationic polymerizations of monomers with phenolic groups were described very seldom in scientific literature (12).

For our investigations we used 4-isopropenylphenol (IPP), 2-methyl-4-isopropenylphenol (MIPP), 2-t-butyl-4-isopropenylphenol (BIPP) and 2.6-di-t-butyl-4-isopropenylphenol (DBIPP) in the cationic copolymerization with CPD. IB was used as termonomer because the properties of the polymers can be changed by its incorporation, but it does not influence the oxygen addition of the CPD structural unit of the copolymer (13). To prevent the gel formation in copolymerizations of a high CPD content in the monomer mixture, the reactions were carried out in toluene as solvent. The more polar solvent dichloromethane was used at low CPD contents in the monomer mixture. The results of the polymerizations are summarized in Tables 1 and 2. You may see that the differently substituted 4-isopropenylphenols were incorporated into the CPD polymers in a remarkable amount, whereby SnCl$_4$ and Et$_3$Al$_2$Cl$_3$ were proved to be very effective initiators. Normally initiator concentrations in the same range as the phenol concentrations are necessary to achieve high yields.

The comparison of the CPD-IB-copolymerization initiated by SnCl$_4$ with the CPD-IB-MIPP-terpolymerization shows that the addition of small amounts of a phenol affects an increase of yield because MIPP as well as IPP and BIPP act as proton active coinitiators besides the residual water present under the conditions described. By this the initiation of the polymerization takes place by initiator-coinitiator-complexes (8). After exceeding a maximum the yield drops if the portion of MIPP in the monomer mixture is increased. This is a consequence of the increasing amount of free MIPP which is not complexed by SnCl$_4$. Furthermore, you may see from Table 2 that the participation if IPP, MIPP and BIPP in the polymerizations generally causes a reduction of the molecular weight. The termination of the growing chain is assumed to take place mostly by C-alkylation of the free ortho-positions of the isopropenylphenols.

Table 1: Polymerization of CPD and IB with 4-Isopropenylphenols

Nr.	Phenol	Monomer Concentration			Initiator	Initiator Concentr. (mmole/l)	Temp. (^oC)
		CPD	IB (mole/l)	Phenol			
1	IPP	0,9		0,1	$SnCl_4$	15	-20
2	MIPP	0,9		0,1	$SnCl_4$	15	-20
3	BIPP	0,9		0,05	$SnCl_4$	15	-78
4	BIPP	0,9		0,05	$Et_3Al_2Cl_3$	2,5	-78
5	DBIPP	0,9		0,03	$SnCl_4$	10	-78
6	DBIPP	0,9		0,03	$Et_3Al_2Cl_3$	2,5	-78
7	IPP	0,45	0,45	0,1	$SnCl_4$	10	-20
8		0,45	0,45		$SnCl_4$	10	-20
9	MIPP	0,45	0,45	0,05	$SnCl_4$	10	-20
10	MIPP	0,45	0,45	0,1	$SnCl_4$	10	-20
11	MIPP	0,45	0,45	0,2	$SnCl_4$	10	-20
12	MIPP	0,45	0,45	0,1	$BF_3.OEt_2$ 1)	20	-20
13	MIPP	0,45	0,45	0,1	$TiCl_4$	5	-20
14	BIPP	0,45	0,45	0,05	$SnCl_4$	10	-78
15	BIPP	0,45	0,45	0,05	$Et_3Al_2Cl_3$	2,5	-78

solvent: toluene (Nr. 1 - 7), CH_2Cl_2 (Nr. 8 - 15)
reaction time: 10 min, 1) 30 min

One can reach higher molecular weights using DBIPP. In this case termination reactions by alkylations are impossible because of the alkyl substituents in the positions 2,4 and 6. This compound shows also a different behaviour with respect to the interaction with the LEWIS acid. As a sterically hindered phenol it should not form complexes with $SnCl_4$ similar to 2.6-di-t-butylphenol (11) and therefore show no cocatalytic activity.

Co- and terpolymers synthesized with the sterically not hindered isopropenylphenols IPP, MIPP and BIPP using the strong LEWIS acids $TiCl_4$ and $Et_3Al_2Cl_3$ show a distinguished lower content of phenols in contrast to the polymers synthesized with $SnCl_4$. The reason for that should be the lowering of the effective concentration of the isopropenylphenols as a consequence of the complexation which takes place to a larger extent.

In the ^{1}H-NMR-spectra of the IPP-CPD-copolymers a broad signal appears between 6.3 and 7.3 ppm which can be attributed to the aromatic protons. A further characteristic signal of the IPP structural unit is that of the methyl group at 1.15 ppm.

Table 2: Polymercharacteristics of the Co- and Terpolymers from CPD, IB and 4-Isopropenylphenols

Nr.	Yield	$\bar{M}_n$	Co- and Terpolymer-Composition (mole-%)		
	(%)	(g/mol)	CPD	IB	Phenol
1	61	n.d.	93		7
2	70	3900	92		8
3	86	n.d.	98		2
4	60	3960	99,4		0,6
5	72	9100	98,7		1,3
6	78	7920	99,1		0,9
7	44	2680	55	37	8
8	28	5600	67	33	
9	54	2500	59	36	5
10	63	n.d.	55	37	8
11	32	n.d.	56	32	12
12	26	2200	73	18	9
13	16	n.d.	50	46	4
14	17	3960	68	27	5
15	23	3230	65	34	1

It will be superimposed by the absorptions of IB centred triades of IB containing polymers. In the proton resonance spectra of the MIP, BIPP and DBIPP-co- and terpolymers one can find absorptions of the alkyl substituents at 2.15 ppm (Me group of MIPP), 1.37 ppm (tBu group of BIPP) and 1.40 ppm (tBu group of DBIPP) in addition to the signals described and those of the CPD and IB units (13). The area of the signals of the aromatic protons is the basis for the calculation of the composition of the co- and terpolymers of IPP and MIPP. In the case of BIPP and DBIPP the areas of the t-butyl group, which can easily be separated from the olefinic protons of CPD and from the aliphatic protons, were used for this determination.

The calculation involves the part of isomerized structural units of CPD, which give rise to a signal at 5.15. ppm (14), whereas the non-isomerized structural units are at 5.6 ppm. The incorporation of the diverse isopropenylphenols can also be proved by the IR spectra of the co- and terpolymers, preferrably by the appearence of the strong OH-stretching band at 3.450 cm^{-1} (ν_{OH}(assoc.)) in the IPP, MIPP and BIPP polymers and at

3,650 cm^{-1} (ν_{OH}(isol.)) in the DBIPP polymers, respectively. Besides one can observe the $\nu_{C-(OH)}$-band, bands of the aromatic ring and of alkyl substituents if the concentration of the phenols is sufficiently high in the polymer.

The uptake of oxygen can be followed up by gravimetry in the case of CPD polymers, because there will be reached a mass increase of about 48 % if one molecule oxygen will be added per CPD unit which could be shown by investigations of the oxidation behaviour of polycyclopentadiene. Therefore, the copolymers were exposed to air at room temperature in a pulverulent thin layer.

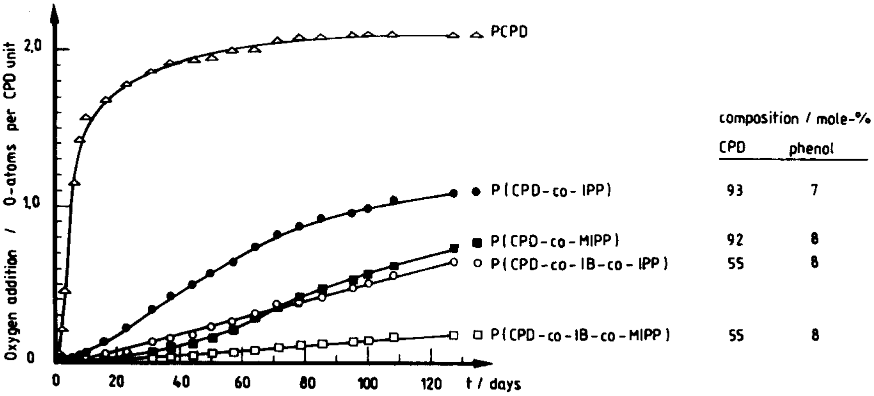

Fig. 1: Influence of Isopropenylphenols on the Oxidation Stability of CPD Copolymers

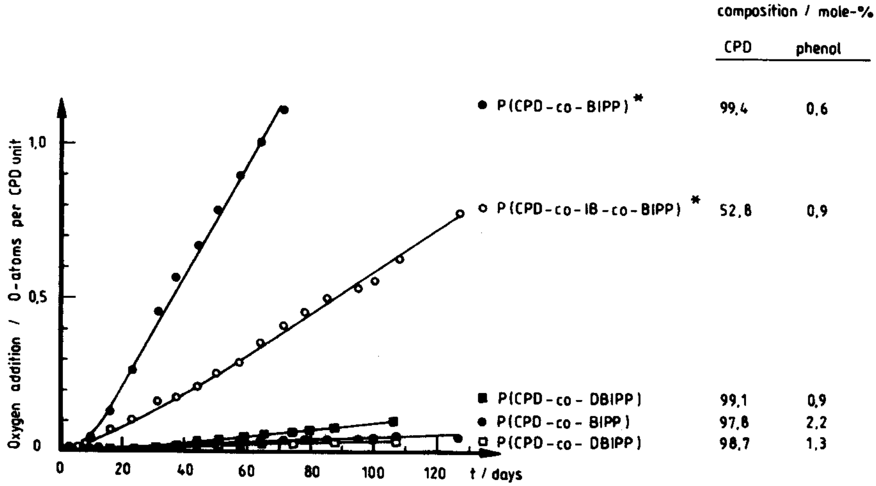

Fig. 2: Influence of Isopropenylphenols on the Oxidation Stability of CPD Copolymers

* Initiator: $Et_3Al_2Cl_3$

From Figures 1 and 2 one can see that all 4-isopropenylphenols used as comonomers inhibit the oxidation of the CPD polymers. Furthermore, the effect of oxidation inhibition of the phenols rises with their concentration in the polymer and the degree of alkylation and the size of the substituents as well. As expected the sterically hindered DBIPP is the most effective antioxidant.

Moreover one can see from Figure 2 that the effectiveness of phenols sterically not hindered as BIPP, depends on the initiator used for the polymerization. In the case of $Et_3Al_2Cl_3$ the effect of the phenol is much lower as in the case of $SnCl_4$ which might be due to a partial deactivation of the OH-group. There was no detailed characterization of the polymers with respect to this fact.

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