Model processing agents for rubber manufacturing

1. Synthesis and characterization of oligomers with different aromatic and cycloaliphatic substituents

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Summary

Oligomers with different aromatic substituents (oligostyrenes, oligo-p-ethyl-styrenes, oligo-p-methoxystyrenes and oligo-1-vinylnaphthalenes) were synthesized by living anionic polymerization using sec-butyllithium as initiator. Number average degrees of polymerization were varied between 2 and 16 and narrow homologue-distributions were obtained. In the case of the benzenic types the isolation into pure homologues from dimers to hexamers was carried out by preparative gel permeation chromatography (GPC). In a polymeranalogous heterogeneous catalytic hydrogenation reaction the aromatic compounds were converted into oligomers with saturated cyclic structures, the initial homologue-distributions not being changed. Characterization of all oligomers was performed by GPC and proton nuclear magnetic resonance (^{1}H–NMR). In the case of oligostyrenes and oligo-p-ethylstyrenes the occurrence of the characteristic high field shift of the ortho-protons is observed in dependence of the degree of polymerization. Oligo-1-vinylnaphthalenes show three differently shielded aromatic resonance areas.

Introduction

Resinous processing agents are commonly used in the practice of rubber manufacturing in order (i) to improve the processibility of highly viscous filled rubber mixtures, (ii) to obtain a higher degree of homogenization of the main constituents of the mixture and (iii) to enhance the performance of the finite product [1]. As the industrially used resins are insufficiently characterized oligomeric multicomponent systems they are not suitable to establish valuable structure-property relationships necessary for obtaining constant quality and high performance products. The selection of adequate resin types in rubber manufacturing is based, still today, rather on simple experience than on well founded scientific criteria. Resins have to be selected according to their solubility, diffusion and partition behaviour in rubber compounds and the way in which they affect surface energies of polymeric phases in blends. A molecular understanding of these effects can only be achieved by the investigation of model resins. Using model resins with well-defined chemical structures and narrow molecular weight distributions, the observed effects in unfilled and filled rubber systems can be

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correlated with the chemical constitution and molecular weight of resins. A taylor made improvement of the processing or the vulcanizate performance can thus become a conceivable target.

The present paper just deals with the synthesis and characterization of model resins with defined aromatic-paraffinic and naphthenic-paraffinic structures.

Experimental part

- Reagents of synthesis

Styrene (99%) and p-methoxystyrene (99%) were obtained commercially. 1-Vinylnaphthalene (97%) and p-ethylstyrene (98%) were synthesized by a Wittig reaction [2]. In the case of 1-vinylnaphthalene the only side product was identified as 2-vinylnaphthalene by GC/MS. The monomeric components were dried over sodium and freshly distilled to make them suitable for anionic polymerization.

Sec-butyllithium (1,3 m solution in cyclohexane) and rhodium (5%) on carbon were used in their commercial grades.

All solvents used for living anionic polymerization were dried over sodium and were freshly distilled.

- Living anionic polymerization

Styrene, p-ethylstyrene and 1-vinylnaphthalene were polymerized living anionically with sec-butyllithium as initiator in toluene + 10 vol.% THF at temperatures between 0 and 20 °C. The polymerization of p-methoxystyrene was proceeded in pure toluene. The monomer concentrations never exceeded 10% (w/v) and the [monomer]/[initiator] ratios were varied between 2 and 16. The polymerizations, being completed, were stopped in all cases with methanol.

- Polymeranalogous hydrogenation reaction

The hydrogenation of oligostyrenes and oligo-p-methoxystyrenes is carried out with oligomers of $\overline{P}_n \leq 10$ in presence of rhodium (5%) on carbon at H_2 pressures of 30 bar and a temperature of 25 °C in cyclohexane. Conversions were accomplished within eight hours. A complete hydrogenation was achieved by the addition of 1,5-8 mol% rhodium relative to the aromatic units.

- Methods of investigation

Analytical gel permeation chromatography: A gel permeation chromatograph (Spectra Physics SP 8100) was used with a column combination PL gel 5 μm; 2*500 Å, 1*100 Å, 2*50 Å. Measurements were performed in THF with sample concentrations of 2% (w/v). Each GPC peak was correlated to the number of main chain segments using a known monomer and dimer as references.

Prepartive gel permeation chromatography: Fractionations were performed on a self-constructed chromatograph with two columns PL gel 10 μm, 100 Å of 60 cm length and 2,5 cm diameter. As a solvent THF was used and sample concentrations were 10% (w/v).

Proton nuclear magnetic resonance: ^{1}H-NMR spectra were recorded at 80 MHz on a Bruker WP 80 SY spectrometer. Sample concentrations were 1-3% (w/v) and measurements were carried out in chloroform-d at 25 °C.

Results and discussions

Living anionic polymerization

The living anionic polymerizations of styrene, p-ethylstyrene, p-methoxystyrene and 1-vinylnaphthalene have been frequently investigated [3] . Oligomeric materials, however, were very seldom of preparative interest in these studies, except oligostyrenes to some extent. When the polymerization is carried out in aromatic solvents (e.g. toluene) sec-butyllithium proves to be the most effective initiator among the butyllithium isomers [4]. The k_i/k_p ratio is additionally increased by the addition of 0,10 to 0,15 mol% Lewis base (e.g. THF) relative to toluene [5]. Within a temperature range of 0 to 20 ° C the addition of THF, however, has no significant effect on the homologue-distributions, as could be shown for oligostyrenes. In consequence to this result the oligomerization of p-methoxystyrene was performed in pure toluene, especially the fact being given that, through the addition of THF, side reactions (e.g. ring coupling by nucleophilic substitution) are greatly increased [6].

Aromatic-paraffinic model resins with theoretical number average polymerization degrees from 3 to 16 were synthesized. According to the described chromatographic conditions oligostyrene and oligo-p-methoxystyrene homologues with purity degrees ≥ 95 % up to hexamers were isolated within two fractionation steps.
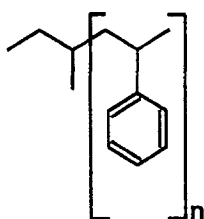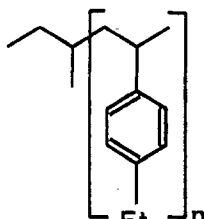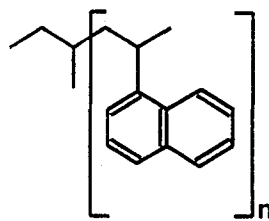
oligostyrenes (OS)   oligo-p-ethylstyrenes (OES)
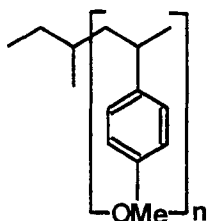
oligo-p-methoxystyrenes(OMS)   oligo-1-vinylnaphthalenes (OVN)

In this paper oligomers are referred to by their abbreviated form together with the corresponding homologue-number of the highest peak from GPC elution curves.

Polymeranalogous heterogeneous catalytic hydrogenation

Following the experimental conditions mentioned above, the catalytic hydrogenations of OS and OMS can be run to any degree of hydrogenation by varying the relative amount of catalyst. No problem of selectivity occurs on the product side, meaning the aromatic units are converted with no exception into cycloaliphatic units.
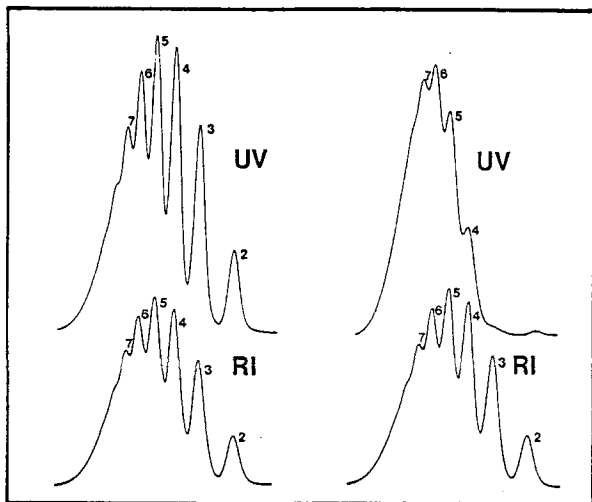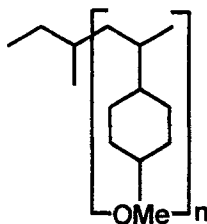

Fig 1: RI- and UV (250nm) detection curves of OS 5 (left) and partially (80%) hydrogenated OS 5 (right)

It is of great importance that the narrow homologue-distributions of the living anionically synthesized aromatic oligomers are not changed by hydrogenation. In no case GPC elution curves, using RI-detection, show a broadening of the distributions or changes of the ratios of distinct homologue-intensities compared to the starting material (Fig.1). The UV-detection curves, however, change characteristically. In consequence of the preferential hydrogenation of the lower aromatic homologues the UV-detection maximum is shifted towards higher peak numbers. Using an excess of catalyst a complete hydrogenation could finally be achieved in all cases.

Naphthenic-paraffinic model compounds with $\overline{P}_n$ values lower than 10 were synthesized.
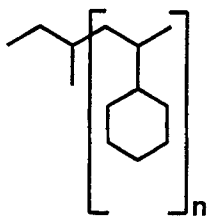
hydrogenated oligostyrenes (h-OS)   hydr. oligo-p-methoxystyrenes (h-OMS)

GPC studies

Homologues up to octamers/nonamers are resolved in the GPC elution curves of the four aromatic oligomer types. Only between monomeric and dimeric homologues a base line separation was achieved (Figs. 2 and 3). The highest elution peaks generally correspond to the theoretically expected molecular weight averages (Fig.2).
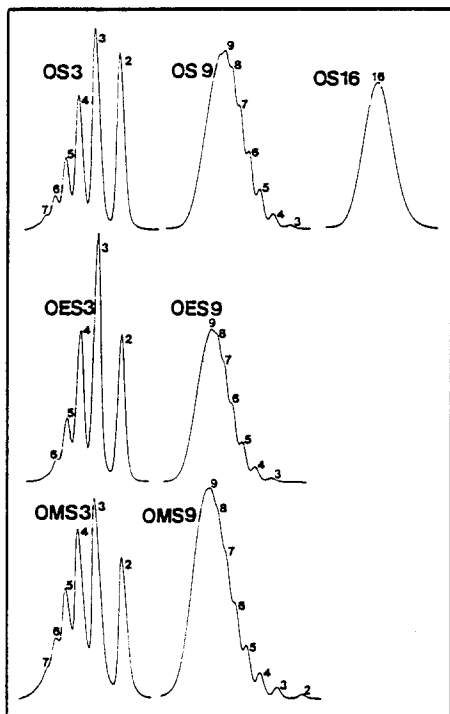

Fig.2: Homologue-distributions of OS, OES and OMS (RI-detection)

OS 3: $\overline{M}n$ = 325
OS 9: $\overline{M}n$ = 950
OS 16: $\overline{M}n$ = 1650
OES 3: $\overline{M}n$ = 410
OES 9: $\overline{M}n$ = 1110
OMS 3: $\overline{M}n$ = 420
OMS 9: $\overline{M}n$ = 1180

In the chromatograms of O-1-VN additional elution peaks or shoulders are resolved besides the main dimeric and trimeric homologues (Fig.3). There is some evidence for the additional peaks (indicated by arrows) to originate from 2-vinyl-naphthalene units in the oligomers.
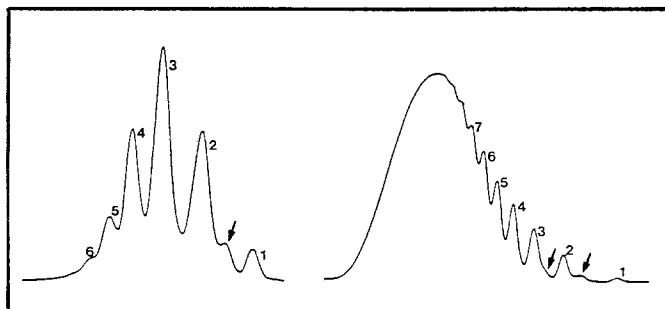

Fig.3: Homologue-distributions of OVN (RI-detection)

OVN 3: $\overline{M}n$ = 520
OVN 10: $\overline{M}n$ = 1600

1H -NMR characterization

Number average molecular weights of OS, OES, OMS and OVN are calculated from the integration of the methyl protons ($\delta < 1$ ppm) of the sec-butyl starter unit (Fig.4). In Figs. 2 and 3 the calculated $\overline{M}_n$ values are shown together with the corresponding homologue-distributions.

From the partial overlap of the α- and β-proton signals at higher oligomerization degrees one can conclude an atactic configuration of OS, OMS and OVN (Fig.4) [7, 8]. In the case of OES the proton signals of the ethyl-substituents partially superpose the α- and β-proton signals and, consequently, a conclusion on tacticity cannot be drawn from the aliphatic proton area.
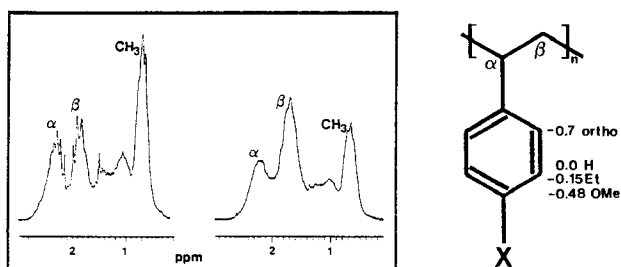

Fig.4: Aliphatic proton spectra of pure OS homologues; nomenclature of carbon atoms and shielding effects (ppm) on aromatic protons

It is a well-known fact that the ortho protons in polystyrenes are particularly high field shifted in consequence of the chain conformation [7]. In Fig.5 the increasing appearance of the resonances of the ortho protons is related to the segment length of pure OS homologues. To underline the effect spectra of poly-disperse systems of higher molecular weight averages are shown in addition. The two aromatic resonance areas of an OS with $\overline{P}_n = 16$ are already fully developed and identical to those of an atactic high molecular weight polystyrene – the integration of the two signals delivering a ratio of 3/2.
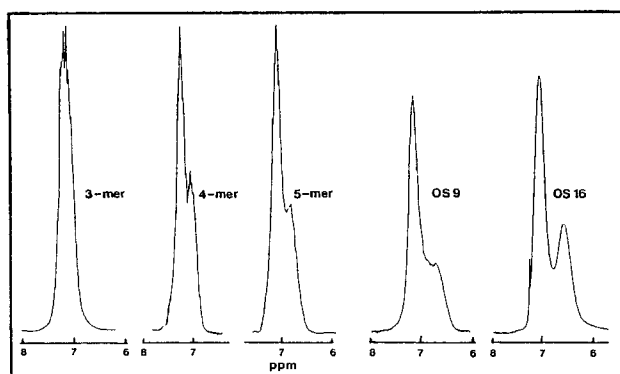

Fig.5: Aromatic proton spectra of pure styrene homologues (3-mer to 5-mer) and polydisperse oligostyrenes (OS 9 and 16)

Aromatic proton spectra of OS, OES and OMS of $\overline{P}_n$ = 9 are compared in Fig.6. The introduction of ethyl and methoxy substituents primarily affects the electron density of aromatic protons in ortho and para positions in comparison to meta positions. The aromatic proton spectra of OES 9 and OMS 9 are well in accordance with the increment data cited in Fig.4. In OES a high field shifted proton area, resulting from the chain conformational effect, is resolved. In OMS all aromatic protons are shielded to about the same extent and a distinction between the shielding effects resulting from the chain conformation and the methoxy substitution is not achieved in the recorded 80 MHz spectra.
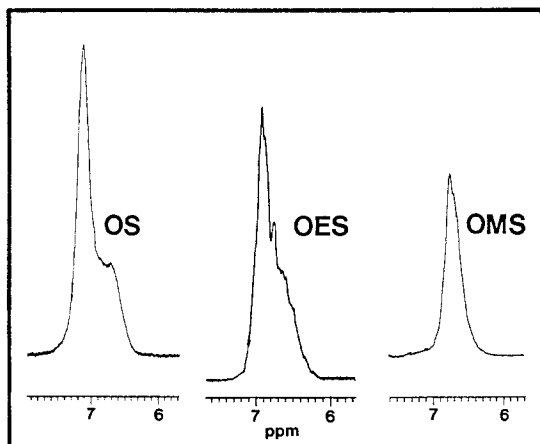

Fig.6: Aromatic proton spectra of OS 9, OES 9 and OMS 9

In poly-1-vinylnaphthalenes three different aromatic proton signals occur [9]. The exact nature of the distinguishible differently shielded protons has not been specified but analogous to the shielding effects in polystyrenes it is expected that protons at the C_2, C_7 and C_8 centres show an excess shielding. In Fig.7 the occurence of distinguishible resonances resulting from excessively shielded protons is shown. At $\overline{P}_n$ = 10 three resonances are distinguishible, although the medium resonance area is only poorly resolved compared to a high molecular weight poly-1-vinylnaphthalene.
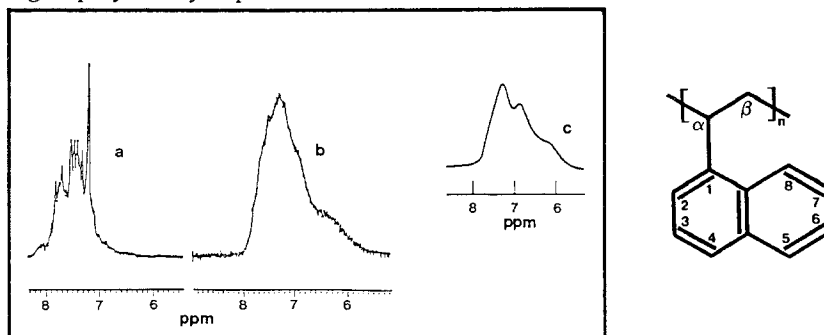

Fig.7: 80 MHz aromatic proton spectra of OVN 3 (a) and OVN 10 (b); 100 MHz aromatic proton spectrum of an atactic poly-1-vinylnaphthalene (c) [9]; nomenclature of carbon atoms in OVN is shown in addition

A forthcoming paper will deal with thermal characterization of oligostyrenes and derivatives.

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