Quarterpolymerizations of Ethene/Propene/Hexene/ Ethylidenenorbornene and Ethene/Propene/Octene/ Ethylidenenorbornene with [Me$_2$C(3-MeCp) (Flu)]ZrCl$_2$ / MAO

Walter Kaminsky (✉), **Ulrich Weingarten**

Institute for Technical and Macromolecular Chemistry, University of Hamburg
Bundesstraße 45, 20146 Hamburg, Germany

Summary

Quarterpolymerizations of ethene/propene/hexene/ethylidenenorbornene and ethene/propene/octene/ethylidenenorbornene were carried out using the catalytic system [Me$_2$C(3-MeCp)(Flu)]ZrCl$_2$ / MAO to determine whether it is possible to lower the glass transition temperature of an EPDM. The influence of the quartermonomer on the polymerization activity and on the product properties, such as the incorporation rates of the three other monomers, the molar mass and molar mass distribution of the polymer were looked at. It was found that the activity is decreased using 1-hexene on the one hand and 1-octene on the other hand as quartermonomer with the effect being more distinct using the former. Both 1-hexene and 1-octene are incorporated to the detriment of propene and ENB, the reduction of the ENB content being more distinct. The molar masses of the polymers are not affected by the substitution of these two monomers by the quartermonomer. The glass transition temperature, however, using 1-hexene or 1-octene, was reduced - in the case of the latter by more than 10 °C from -50 to -62 °C.

Introduction

Ethene/propene/diene terpolymers (EPDM) are commercially important elastomers[1,2]. Their glass transition temperature is determined by their composition[3], i.e. the amounts of the monomers and the nature of the termonomer. Besides ENB other tercomponents, such as dicyclopentadiene[4] or hexadiene (1,4-HD)[5], are used. Since the glass transition temperature defines the limit of application for an elastomer, it is desirable to have a material with a very low glass transition temperature so that the range of exterior applications, as demanded by the building and automobile industry, can be expanded. With polyhexene having a glass transition temperature of -35 °C and polyoctene having one of even -60 °C, the use of hexene or octene as a substitution for propene, the polymer of which has a glass transition temperature of -4 °C, should be a good possibility to lower the glass transition temperature of EPDMs.

Experimental

All procedures were carried out under argon using Schlenk techniques.
Materials:

MAO was purchased from Witco, ethene from Linde and propene from Gerling, Holz &
Co. The gases were purified by passage through columns with Cu catalyst (BASF R3-
11) and molecular sieve of 10 Å. 1-hexene and 1-octene were purchased from Merck
with purities $\geq$ 96 % in the case of the former and $\geq$ 97 % in the case of the latter. The
liquidous monomers were degased and dried over triethylaluminium (Witco) in the case
of 1-hexene or refluxed over calcium hydride in the case of
1-octene, for one week and distilled.

Toluene was refluxed over Na/K for several days and distilled before use. ENB
(Aldrich) was dried over triisobutylaluminium (Witco) and distilled prior to use.
Polymerizations:

Polymerizations were carried out in a 1 l Büchi AG type I autoclave equipped with an
additional cooling system. Feed of the gaseous monomers was maintained with a Peteric
3002 pressflow controller. The reaction was monitored by a Büchi data system bds 488.
For the standard experiment, the reactor was evacuated at 95 °C for 1 h, then cooled
down to the polymerization temperature of 30 °C, charged subsequently with 800 mg
MAO, the required amount of ENB, hexene or octene and toluene leading to an overall
volume of 400 ml. Ethene and propene were added afterwards, so that the total
monomer concentration was 1 mol/l. The molar fractions of the liquid monomers were
adjusted using their densities, the gasous monomers were adjusted using the data given
in[6], assuming that the solubility in the feed is the same as in pure toluene.
Polymerization was started by injection of toluenic metallocene solution. During the
polymerization the total pressure was kept constant by supplying ethene. The
polymerization was quenched by addition of 5 ml of a saturated solution of 2,6-di-*tert*bu-
4-methylphenol in ethanol. The polymer solution was stirred overnight with dilute
hydrochloric acid followed by neutralization with $NaHCO_3$, washing with water,
evaporation of toluene and drying. About 1 g of polymer was obtained, with values
below 5 % conversion rates for all comonomers were kept low.
Polymer analysis:

Incorporation rates were determined by IR and ^{13}C-NMR spectroscopy. The NMR
samples were prepared by dissolving the polymers (10 mass%) in a mixture of
perchlorobutadiene (PCB) and 1,1,2,2-tetrachloro-1,2-dideuteroethane (TCE-d$_2$) and
measured at 100 °C on a Bruker 300 MHz NMR instrument. First the relative amounts
of ethene, propene and ENB were calculated from the IR-spectra using the bands at 720
and 1160 cm^{-1} for ethene and the band at 1688 cm^{-1} after smoothing and derivating two
times for ENB. The relative amount of propene is given by the difference to 100 %.

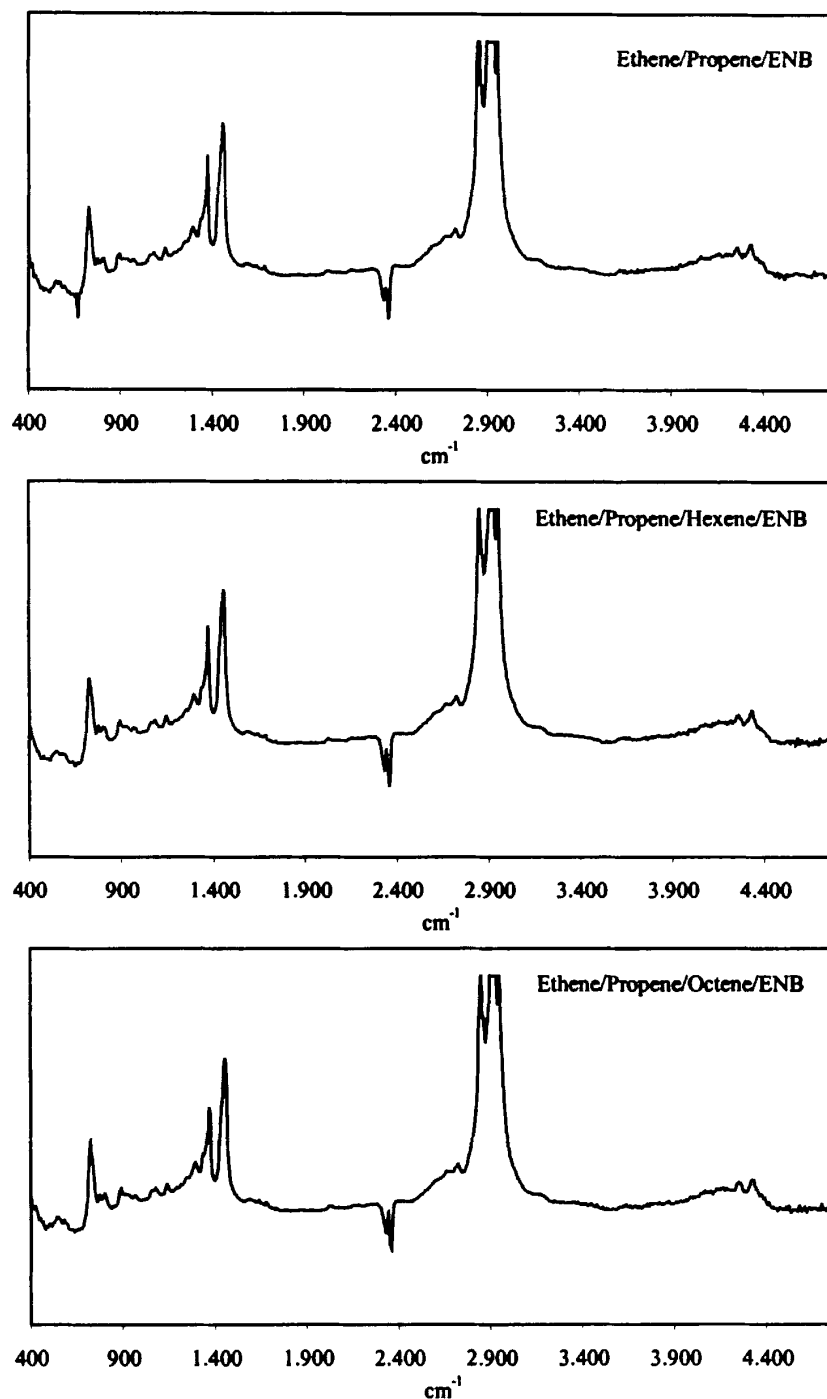Figure 1: IR spectra of ter- and quarterpolymers

Then the amount of hexene or octene relative to the other three was calculated from the ^{13}C-NMR-spectra. The separatable $2B_4$-signal in the case of hexene and the $2B_6$-signal in the case of octene were taken for the calculation. In the case of octene the result was controlled using the other separatable signal: $3B_6$. By standardisation to 100 %, the absolute amounts of all four monomers were received.
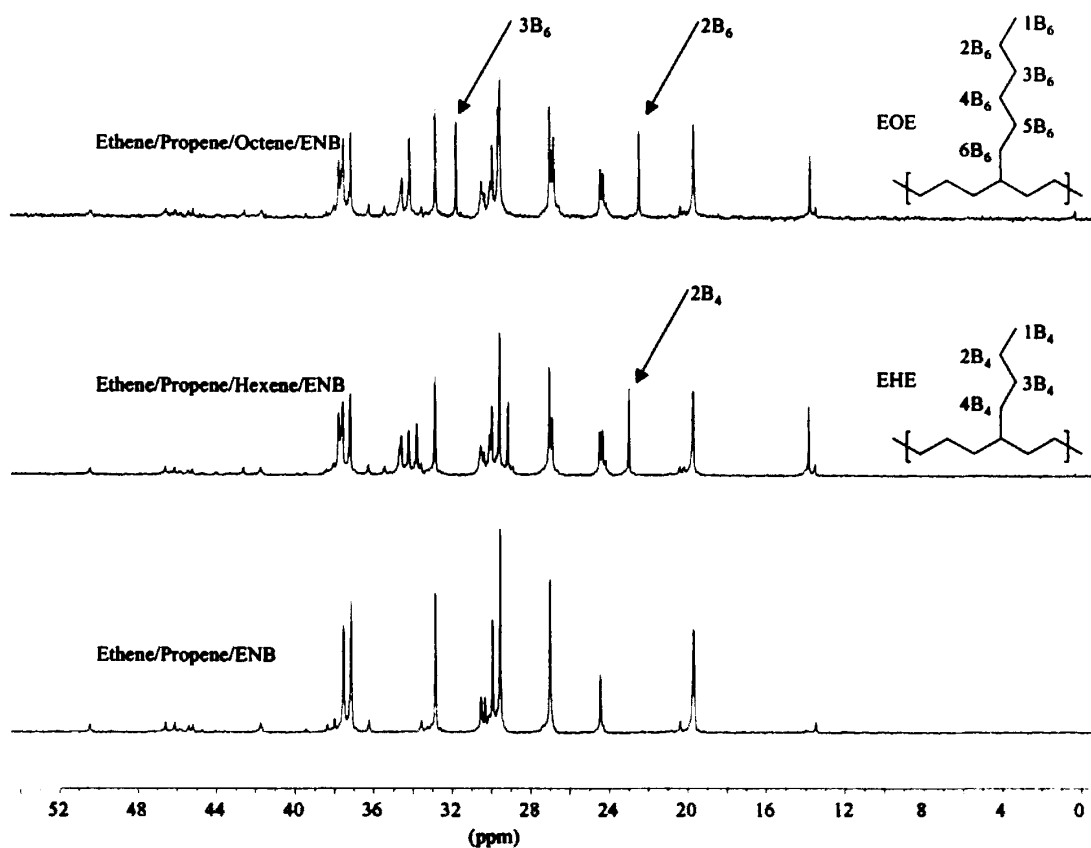
454

Figure 2: ^{13}C-NMR spectra of ter- and quarterpolymers

The molar masses M_η were determined using an Ubbelohde viscosimeter (capillary 530 0a, K = 0,005 mm^2/s^2), the samples were prepared by dissolving 50 mg of polymer in 50 ml of decahydronaphtalene (stabilized with 1 g/l 2,6-di-^{tert}bu-4-methylphenol) and measured at 135 °C. As the Mark-Houwink constants for the EPDMs are unknown all molar masses are calculated using the values for PE, which were taken from the literature[7]. Molar mass distributions were determined by gel permeation chromatography on a Waters high temperature 150-C-ALC/GPC instrument (1,2,4-trichlorobenzene, 135 °C) using a PL-EMD-960 evaporation light scattering detector. Differential scanning calorimetry was performed on a DSC-4 from Perkin-Elmer. To eliminate any thermal history, the samples (10 mg) were heated to 200 °C, cooled at -320 °C/min to -100 °C and heated to 200 °C with a heating rate of 20 °C/min. The values of the second run are reported.

Results and Discussion

Activity

From the data given in Table 1 it is obvious that the polymerization activity is decreased with an increasing amount of the higher α-olefin, i.e. 1-hexene or 1-octene. The effect is more distinct with the former.

Table 1: Activities in quarterpolymerizations of ethene/propene/α-olefin/ENB, molar masses and glass transition temperatures of the resulting products

run #	X_{ethene}	$X_{propene}$	$X_{\alpha\text{-olefin}}$	X_{ENB}	activity	M_η g/mol	T_g [°C]
1	0,3	0,6	-	0,1	13000	20000	-50
2	0,18	0,36	$0,4_h$	0,06	7800	21000	-54
3	0,06	0,12	$0,8_h$	0,02	3800	20000	-53
4	0,18	0,36	$0,4_o$	0,06	10000	16000	-55
5	0,06	0,12	$0,8_o$	0,02	4200	18000	-62

a) $kg_{pol}/(mol_{Zr}{*}h{*}mol_{mon}/l)$, $_h$ = 1-hexene, $_o$ = 1-octene, $X_{...}$ = molar fraction of ethene, propene, α-olefin, ENB in the feed

Incorporation of the monomers

Two aspects are of interest: On the one hand, it has to be ascertained if and how the ratios of the monomers ethene, propene and ENB are changed in respect to each other by the incorporation of the higher α-olefin and, on the other hand, how large the quantity of incorporated higher α-olefin is. Table 2 gives the answers to these questions.

Table 2: Incorporation rates of ethene, propene and ENB in quarterpolymerizations of ethene/propene/α-olefin/ENB standardized to x_{ethene} + $x_{propene}$ + x_{ENB} = 100 mass%, absolute incorporation rates of all monomers in quarterpolymerizations of ethene/propene/α-olefin/ENB

run #	X_{ethene} [stand. mass%]	$X_{propene}$ [stand. mass%]	X_{ENB} [stand. mass%]	X_{ethene} [mass%]	$X_{propene}$ [mass%]	$X_{\alpha\text{-olefin}}$ [mass%]	X_{ENB} [mass%]
1	56	36	8	56	36	-	8
2	59	33	8	45	25	24_h	6
3	73	22	5	31	9	58_h	2
4	60	32	8	44	24	26_o	6
5	83	13	4	30	5	64_o	1

$_h$ = 1-hexene, $_o$ = 1-octene, $X_{...}$ = molar fraction of ethene, propene, α-olefin, ENB in the polymer

On the one hand the amounts of ethene, propene and ENB in the polymer are given in mass% standardized to x_{ethene} + $x_{propene}$ + x_{ENB} = 100 mass% for a better comparability of the ratios with that of the terpolymer and on the other hand the absolute values for all four components are given. It is clear from the data given in Table 2 that hexene as well as octene is incorporated to the detriment of propene and ENB. The incorporation rate of the higher α-olefin increases with an increasing amount of the monomer in the feed composition. With 40 mol% of the feed composition consisting of the higher α-olefin, hexene and octene are incorporated in the same order of magnitude. With 80 mol% of the higher α-olefin in the feed octene is found in a greater amount in the polymer than hexene in the comparable product. This is due to the fact that the molar mass of octene is one third higher than that of hexene. Both of these monomers displace ENB to a higher degree than propene.

Molar masses

As is clear from the data given in Table 1, there is no effect on the molar masses of the polymers, i.e. the molar masses of the quarterpolymers are independent of the amount and the type of quartermonomer used.

Melt and glass transition temperatures

As one would expect, no crystallinity was detected in the described range of monomer compositions.

The glass transition temperature can be decreased by addition of both quartermonomers, hexene and octen respectively. Using hexene as quartermonomer a minimum glass transition temperature of – 54°C is reached. Going to higher amounts of hexene in the polymer, the glass transition temperature rises again. This is due to the fact that with a further increase of the incorporation of hexene not only propene and ENB are displaced, the homopolymers of which have higher glass transition temperatures than polyhexene, but also rising degree of ethene. The glass transition temperature of polyethylene is clearly below that of polyhexene, so that the glass transition termperature rises again with an increasing amount of hexene in the polymer – in the borderline up to the value for the homopolymer of hexene (about – 35°C). Using octene as quartermononomer, a glass transition temperature of – 62°C is reached which means a decrease of 12°C compared to EPDM terpolymer. Adding more octene, the glass transition temperature should not reach values clearly below this because the value for the homopolymer of octene is about – 60 °C.

It is apparent that the route described in this paper works in the sense that the glass transition temperature can be reduced by the addition of higher α-olefins without affecting the molar masses of the resulting polymers. Starting with an EPDM that has medium contents of propene and ENB, in industrial terms,the products with the best glass transition temperatures have alow diene content. The amount of propene inocorporated is also decreased but the elastomeric properties are conserved because of the higher α-olefin. Another way to reduce the glass transition temperature of EPDMs is to use another termonomer, such as 1,4-hexadiene, that has better properties than ENB in respect to the glass transition temperature but has the drawback of being very expensive.

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