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MOLECULAR WEIGHT DETERMINATION FOR 1,2,1,2-POLYPROPADIENE

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Abstract—By using standard bromination conditions, the insoluble 1,2,1,2-polypropadiene (formed by $Ni(acac)_2$ or $Co(acac)_{2 \text{ or } 3}$, C_3H_4, $(iBu)_3Al$ catalysts) is transformed into a soluble bromopolypropadiene. Using this technique, determination of molecular weight becomes possible. It was found that the molecular weight increases with polymerization time until a steady value is reached. As the polymer yield continues to increase when a constant molecular weight has been reached, chain transfer must occur. The molecular weight of polybromopropadiene was independent of the concentrations of the catalyst components. From experiments with crosslinked polymers and from theoretical considerations, it was deduced that the low solubility of the original 1,2,1,2-polypropadiene is due to its high crystallinity.

INTRODUCTION

Polypropadiene of highly regular structure can be prepared by Ziegler-catalysts [1, 2] or Rh (I) complexes [3]. This polymer is only slightly soluble in solvents such as boiling toluene, chlorobenzene or xylene [1].

Baker [4] and Havinga [5] also obtained only slightly soluble polymers. Otsuka [6] verified this Ziegler-type polymerization with $Ni(acac)_2$ Et_3Al and claimed that he obtained an insoluble gel. With π-allylnickel complexes no gel was formed, and this was proposed as the explanation of the good solubility of this polymer. Tadokoro [7] found that the Ziegler-type polymer was more regular than the π-allyl type. van Ommen *et al.* [8, 9] showed that bis-π-allyl-nickel gives a polymer, with the same i.r.-spectrum as polymers formed with catalysts based on $Ni(acac)_2$ [8] or $Co(acac)_2$ [9], provided the monomer is added to the catalyst before the aluminium alkyl. They also showed [8, 10] that the same polymers as synthesized by Otsuka [6] could be obtained by adding pyridine [8] to the Ziegler-catalysts or by using π-allylnickel chloride [10]. The polymer thus obtained contains the

$$1, 2, 1, 2\text{-}(-CH_2-C-CH_2-C-)_n$$
$$\qquad\qquad \underset{CH_2}{\overset{\|}{}} \qquad \underset{CH_2}{\overset{\|}{}}$$
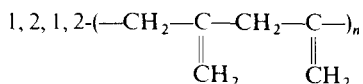
and the conjugated 1, 2, 2, 1-structural elements

$$(-CH_2-C \text{——} C-CH_2-)_n$$
$$\qquad \underset{CH_2}{\overset{\|}{}} \quad \underset{CH_2}{\overset{\|}{}}$$
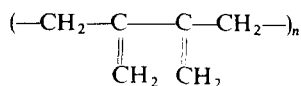
as shown by i.r.-spectra [7, 8]. This irregularity of the polymer chain could be the cause of the good solubility of Otsuka's polymer [6, 11]. Therefore it is not yet clear whether gel formation resulting from crosslinking or high crystallinity is the cause of the low solubility of highly regular 1,2,1,2-polypropadiene. This is one reason why a good method to determine

the molecular weight of the 1,2,1,2-polypropadiene was sought. The other reason is that the result could give insight into the mechanism of the polymerization, by measuring the molecular weight as a function of polymerization time, and of the Al-and Ni-concentrations.

MOLECULAR WEIGHT DETERMINATION

For determination of the molecular weight of a polymer, solubility is a primary condition. As stated already, there is no good solvent for crystalline 1,2,1,2-polypropadiene prepared by Ziegler-catalysts. One of the reasons could be the easy cross-linking of the polymer by oxygen as noticed already by Havinga [5]. In the kinetic experiments [10], it was observed that, even in a N_2 atmosphere, it was not possible to dissolve an appreciable amount of polymer at room temperature, once it had precipitated.

By addition to the double bonds in the polymer, an attempt was made to improve the solubility and stability to crosslinking by O_2. Hydrogenation did not give reproducible results. HCl added only to part of the double bonds and left the polymer still difficult to dissolve. By using Cl_2, not only the unsaturated double bonds disappeared but also the molecular weight decreased dramatically with chlorination time. It was found in the literature [14] that, in the bromination of butyl-rubber, the breakdown was relatively small compared with that during chlorination. Although butylrubber has only 3–5% unsaturated groups and is therefore not the best comparison for 1,2,1,2-polpropadiene, it was decided to investigate the possibility of using bromination in order to obtain a more readily soluble and stable polymer.

EXPERIMENTAL

Preparation of polybromopropadiene

The polymerization was performed as described earlier [1]. If toluene was used as solvent it was evaporated com-

Table 1. Molecular weights of bromopolypropadiene as a function of bromination time and catalyst composition. Polymerization time 24 hr

$C_{Ni\ or\ Co(acac)_2}$ (mol l^{-1})	Al/Ni(Co)	Bromination time (hr)	Osmometry ($\bar{M}_n \times 10^{-3}$)	$\bar{M}_n \times 10^{-3}$	GPC $\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
$22 \cdot 10^{-4}$	100	5	16	16	32	2
$44 \cdot 10^{-4}$*	36	20	17	18	27	1.5
$44 \cdot 10^{-4}$*	36	20	19	19	27	1.4
$44 \cdot 10^{-4}$*	36	20	18	19	27	1.4
$40 \cdot 10^{-3}$	5.5	1		15	32	2.1
$40 \cdot 10^{-3}$	5.5	2		14	25	1.8
$40 \cdot 10^{-3}$	5.5	5		14	24	1.7
$40 \cdot 10^{-3}$	5.5	22		11	19	1.7
$40 \cdot 10^{-3}$	5.5	48		11	19	1.7
$40 \cdot 10^{-3}$	2	20		16	28	1.8
$40 \cdot 10^{-3}$	3.4	20		14	23	1.6
$40 \cdot 10^{-3}$	9	8		13	23	1.8
$40 \cdot 10^{-3}$	9	24		12	20	1.7
$40 \cdot 10^{-3}$	9	20		12	21	1.8
$44 \cdot 10^{-4}$*	36	20		27†	52†	1.9

* $Co(acac)_2$.

† Bromination in air, $\bar{M}_n$ and $\bar{M}_w$ are determined for the soluble part.

pletely and then 10–15 ml dried, O_2 free, benzene were added to about 0.5 g of the polymer; the reaction vessel was then cooled to 6°. 5–6 ml of pure Br_2 were then added dropwise. The polymer was stirred with the Br_2 for 8 hr at 0° and filtered to remove the catalyst. Up to this point, it was essential to work under an O_2-free atmosphere otherwise there was crosslinking. The solution of polybromopropadiene in benzene thus obtained was added to 50 ml of diethylether. The polymer precipitated and was filtered and washed with about 500 ml diethylether until the washings were colourless. The polymer was then dried at room temperature and 0.1 mm Hg.

Molecular weight determination

Gell permeation chromatography (GPC) determinations of $\bar{M}_n$ and $\bar{M}_w$ were performed on a Waters 4-column instrument. The column length was 4 ft. per column, o.d. 3/8 in. and the porosity sequence of the cross-linked polystyrene packing (Stryra gel) 10^5–3.10^4–10^3–250 Å. The eluant was tetrahydrofuran (Baker p.a.) (a good solvent for polybromopropadiene), the flow rate 1 ml min^{-1}, the temperature 30° and the syphon volume 5.58 ml. Polymer solutions (0.25%) were injected in 40 sec and detected with a refractivity increment.

The relation between elution volume and $\bar{M}_n$ was established by determination of $\bar{M}_n$ for several samples by means of a Hallikainen automatic membrane-osmometer. The membrane was Sartorius SM11539 (ultracella "allerfeinst"). Five polymer solutions of concentrations between 0.1 and 0.5% in toluene (Merck p.a.) were examined at 25°. An empirical correction for peak-broadening (determined for a series of standard polystyrenes) was applied: $(\bar{M}_n)GPC = 1.20 \times (\bar{M}_n)$true, $(\bar{M}_w)GPC = 1.00 \times (\bar{M}_w)$true.

Elemental analyses were performed by the Organic Chemical Institute TNO, Utrecht, The Netherlands.

RESULTS

Bromination of the 1,2,1,2-polypropadiene produced a soluble polymer and, according to the i.r.-spectrum, almost all double bonds disappeared (1635–890 cm^{-1} [7]) while the —CH_2— groups remained unchanged (1420 cm^{-1} [7]).

The NMR spectra show, in agreement with the i.r. spectra, that the broad absorption of the =CH_2 group at $\delta = 5$ ppm disappears after a short bromination time, while at $\delta = 4.5$ ppm a new broad absorption appears, attributed to the —CH_2Br group. The broad absorption of the —CH_2— group in the polymer chain at $\delta = 2.5$ remains unchanged during the bromination.

There was only a small tendency for decrease in molecular weight during bromination, see Table 1. This result is only obtained under mild conditions, viz. 6° and low Br_2 concentration. If the temperature is increased to 25° and Br_2 is not diluted by benzene, a large decrease of molecular weight is observed ($\bar{M}_n = 1600$). This last observation casts some doubt on the relation between the molecular weight of bromopolypropadiene and that of the original polypropadiene. However, the reproducibility of the results (see Table 1) suggests that the molecular weights of the bromopolypropadiene are indeed representative for those of the original polymer.

The elemental analysis of the bromopolypropadiene is not in agreement with the expected theoretical values (Table 2). However, after 2 hr, the molecular weight of one unit is constant (165) within $\pm 3\%$. This can be explained by assuming that part of the added bromine is eliminated again as HBr. The formation of this compound during bromination was actually observed, also in accordance with the results of the bromination of butylrubber [14].

Renewed addition of a second molecule Br_2 followed by a second elimination of HBr is also possible. In agreement with this, it was found that prolonged bromination led to a new absorption in the i.r.-spectrum, attributed to this brominated double bond (1670 cm^{-1}). In agreement the NMR spectra showed broad absorptions at $\delta = 7$ ppm and $\delta = 7.5$ ppm which could be attributed to the —$CHBr_2$ and the =CHBr group repectively.

If bromination is not performed in an inert atmosphere, the molecular weight increased and the i.r.-spectrum of the product showed a $>C=O$ absorption at 1700 cm^{-1} and a C—O—C absorption at

Table 2. Elemental analysis of bromopolypropadiene

	Bromation time (hr)	Formula	$\overline{M}_n$ per unit
Experimental			
	1	$C_3H_{3.8}Br_{1.50}$	159.7
	2	$C_3H_{3.38}Br_{1.59}$	166.4
	5	$C_3H_{3.40}Br_{1.54}$	162.4
	22	$C_3H_{2.83}Br_{1.59}$	165.9
	48	$C_3H_{2.53}Br_{1.65}$	170.4
			Mean value 165 ± 5
Theoretical			
1. Full bromation		$C_3H_4Br_2$	199.8
2. Elimination of HBr		C_3H_3Br	118.9
3. Addition of a second Br_2		$C_3H_3Br_3$	278.7
4. Elimination of a second HBr		$C_3H_2Br_2$	197.8

$$1. \underset{CH_2Br}{(-CH_2-\overset{Br}{\underset{|}{C}}-)_n.} \qquad 3. \underset{CHBr_2}{(-CH_2-\overset{Br}{\underset{|}{C}}-)_n.}$$

$$2. \underset{CHBr}{(-CH_2-C-)_n.} \qquad 4. \underset{CBr_2}{(-CH_2-C-)_n.}$$

$1110\,cm^{-1}$, indicating that part of the polypropadiene is oxidized and crosslinked and the polymer thus obtained is only partly soluble. Table 1 also shows that the Al/Ni ratio has little influence on $\overline{M}_n$ if polymerization proceeds for 24 hr. Table 3 shows that, especially at the beginning, the molecular weight of the polymer and the spread $(\overline{M}_w/\overline{M}_n)$ increase with polymerization time.

DISCUSSION

From the results obtained with high Br_2 concentrations, it follows that chain breakdown can occur. The relatively low molecular weight of about 16,000, corresponding to a chain length of about 100 monomer units and obtained under mild bromination conditions, is therefore somewhat uncertain. The fact remains, however, that unlike the case with Cl_2, the results are reproducible. From theoretical considerations [15] it follows that highly crystalline isotactic polystyrene with a chainlength of only 20 monomer units is almost insoluble, if the mixture of the solvent with the molten polymer is ideal, i.e. no heat or volume changes occur. It is also known that 1,2-poly-

Table 3. Influence of polymerization time on the molecular weight of 1,2,1,2-propadiene obtained by a $Ni(acac)_2$ $(6 \cdot 10^{-3}\,mol\,l^{-1})Al/Ni = 50$ catalyst at 25° in toluene

Polymerization time (min)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
6	3	4	1.3
15	7.4	10–12	1.6
22.5	--	12	--
30	8.6	15	1.7
60	9.0	16	1.8
24 hr	13	23	1.8

butadiene, with a structure similar to that of 1,2,1,2-polypropadiene, neither of which are elastomers, is also highly crystalline and almost insoluble and there is no indication that its insolubility is due to crosslinking [16].

The observation that cross-linking occurs if the bromination is carried out in contact with air, resulting in a much higher molecular weight for the soluble part of the polymer, gives a strong indication that Br_2 is not capable of breaking down a cross-linked polymer.

It was also observed that, during polymerization in the absence of O_2, the polymer precipitated slowly from the solution. Once precipitated, however it could not easily be redissolved although bromination of this polymer produces a soluble product.

These results strongly suggest that the low solubility of the 1,2,1,2-polypropadiene results from high crystallinity [7]. This high crystallinity is also deduced from X-ray powder diffraction (see Fig. 1). The increase in solubility in various solvents upon addition of Br_2 to the double bonds can be explained on the one hand by the loss of stereoregularity and the bulkiness of the Br atoms and on the other hand by the increased polarity causing a larger solvation energy. The brominated polymers are stable on exposure to air: even after 80 days $\overline{M}_n$ and $\overline{M}_w$ have not changed.

The reproducible results of the molecular weight determinations for polybromopropadiene indicate that these values are representative for the original 1,2,1,2-polypropadiene. In that case, Table 3 shows that the molecular weight of 1,2,1,2-polypropadiene increases with polymerization time.

If it is supposed that all Ni atoms are active in the polymerization and that these continue chain growth until an average length of about 100 units is obtained, we are able to calculate, using a value of $4.2\,min^{-1}$ for k_p as obtained from previous kinetic measurements
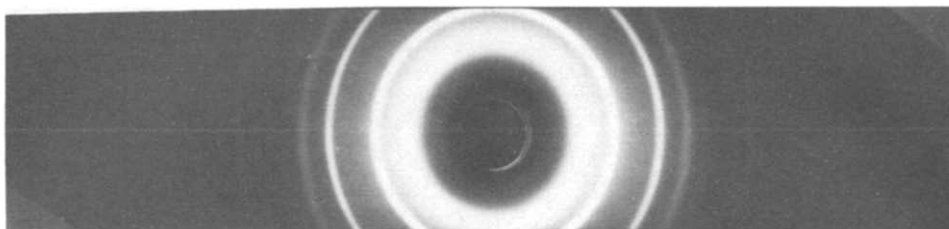
Fig. 1. X-ray powder diffraction pattern of 1,2,1,2-polypropadiene.

(k_2 in Ref. [10]), the molecular weight to be expected after a certain time.

Time	$\overline{M}_n$ observed	$\overline{M}_n$ calculated
6	3000	4000
15	7400	10,000
30	8600	22,000
60	9000	41,000

For the first 15 min, there is reasonable agreement between the observed and calculated values of $\overline{M}_n$; the agreement might even improve if it is noted that deactivation lowers the polymerization rate constant to a final value of $0.84\,min^{-1}$ [10]. This suggests that all Ni atoms are active centres for chain growth, with the same rate constant, at the start of the polymerization. If the polymerization is stopped at short times ($<15\,min$) we must find a low $\overline{M}_n$ and a narrow $\overline{M}_w/\overline{M}_n$ in agreement $\overline{M}_w/\overline{M}_n = 1.3$ at $t = 6$ min. The molecular weight becomes nearly constant for long polymerization times (Table 3), while polymer yield still increases. This suggests that termination of the chain growth occurs, possibly by crystallization of the polymer, after a certain length (100 monomer units) has been reached. Because termination does not take place at exactly the same chain length, $\overline{M}_w/\overline{M}_n$ must increase a little with time (Table 3).

This termination may occur in different ways if the catalyst is considered. One possibility is that only part of the Ni complexes formed after chain termination are active and able to start growth of a new chain while the rest remains inactive. The inactive part is not encapsulated in the polymer, as shown by Ni-determinations in polymer and solvent [10]. This would lead to an apparent decrease of k_p with time and a relatively small increase in $\overline{M}_w/\overline{M}_n$. In this case, the decreasing rate constant [10] shows that a decreasing amount of Ni complexes is active in the polymerization. A second possibility is that, as proposed originally [10], the C_2-bimetallic Ni–Al catalyst–complexes are converted into less active complexes called C_3 after termination of the chain growth. These C_3-complexes must then produce 1,2,1,2-polymer chains at a lower rate but with approximately the same molecular weights as the C_2-complexes because $\overline{M}_n$ becomes nearly constant.

It is observed that, after prolonged polymerization (24 hr), the polymer yield is still increasing, which would not be expected if every Ni-atom could produce only one polymer chain. The yield of polymer, however, depends on C_{Ni} and on the ratio Al/Ni [1, 10] which can also be explained by both mechanisms proposed above.

CONCLUSIONS

(i) With standardized bromination conditions, it is possible to obtain information about the dependence of the molecular weight of 1,2,1,2-polypropadiene on polymerization time and on catalyst composition.

(ii) The molecular weight increases with polymerization time up to a constant final value.

(iii) As the polymer yield increases with time while the molecular weight becomes constant, chain transfer must take place.

(iv) The molecular weight is independent of the Al and Ni concentrations and also the use of Co instead of Ni has only a small influence.

(v) The insolubility of 1,2,1,2-polypropadiene in the absence of O_2 is probably caused by the high crystallinity of this polymer and not by cross-linking.

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