Optically active polymers via ring-opening metathesis polymerization: 1. Polymers from enantiomerically pure 2-acyloxybicyclo[2.2.1]hept-5-enes*

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The ring-opening metathesis polymerization (ROMP) of enantiomerically pure 2-substituted norbornenes carried out with $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ in chlorobenzene or with $K_2[RuCl_5(H_2O)]$ in aqueous solvents leads to polymers that show optical activity. The increasing specific rotations of the polymers from acetate to butyrate to benzoate with both catalysts is explained by increasing substituent group size.

(Keywords: optical activity; polynorbornene derivatives; ROMP)

INTRODUCTION

Optically active polymers have been of great interest over the last few years. On the one hand, these polymers can be applied as chiral stationary phases in liquid or gas chromatography. On the other hand, such polymers are of great importance in the investigation of polymerization mechanisms.

Optical activity in polymers can be achieved by three means:

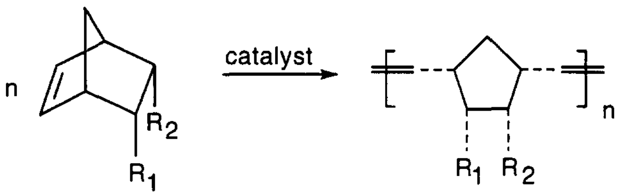
(1) Optical activity is the result of chiral centres in the main chain. For example, Consiglio and Waymouth studied the formation of optically active poly(methylene-1,3-cyclopentane) from 1,5-hexadiene using a chiral zirconium-based Ziegler–Natta catalyst[1]. Other polymers of this type were investigated by Wulff and Wu[2,3].

(2) Optical activity resides in the side chain. Moore *et al.* synthesized soluble, chiral polyacetylenes via ring-opening metathesis polymerization (ROMP) of cyclooctatetraenes with a chiral side group[4]. Liu and coworkers synthesized chiral polymers containing the acetoxybornyl group and demonstrated their application in asymmetric induction[5].

(3) Optical activity results from a supermolecular structure. The largest group of optically active polymers derive their chirality from the single-handedness of the helices they form. Thus Okamoto and Hatada described the synthesis and use of optically active poly(triphenylmethyl methacrylate) (PTrMA) as chiral stationary phases for use in gas or liquid chromatography[6]. Together with Vogl they investigated the initiation of anionic asymmetric polymerization[7]. Likewise Lifson and coworkers studied the steric effects in helical poly(n-alkyl isocyanates) and found evidence of helix inversion[8]. Derning and Novak showed the living polymerization of isocyanides[9]. The polymers, besides showing helicity, mimicked biological properties.

At this time the main disadvantage of commercially available chiral stationary phases prepared from PTrMA is their limited stability towards certain solvents owing to the lack of crosslinking[6]. In order to increase stability by providing crosslinks, polymers with main-chain unsaturation would be expected to be useful. The ring-opening metathesis polymerization (ROMP) of chiral 2-substituted bicycloalkenes leads to such polymers where a ring is embedded between two crosslinkable vinylene groups.

In this paper we describe the synthesis of optically active polymers via ROMP of norbornene derivatives of high enantiomeric purity (*Scheme 1*).



polymer a:	R_1 = OAc	R_2 = H
polymer b:	R_1 = OBut	R_2 = H
polymer c:	R_1 = OBz	R_2 = H
polymer d:	R_1 = H	R_2 = OAc
polymer e:	R_1 = OAc,H	R_2 = H,OAc (racemic)

Scheme 1

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EXPERIMENTAL

$\mathrm{Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2}$ was donated by and used as received from Professor R. R. Schrock (MIT, Cambridge, Mass.), and $K_2[RuCl_5(H_2O)]$ was used as bought from Aldrich.

endo-Norborn-5-ene-2-butyrate was provided by Christian Doppler Laboratorium für Chirale Verbindungen, Enzymatische und Mikrobielle Synthese, Graz.

The preparation of 7-oxanorbornene-2,3-dicarboxylic acid dimethyl ester is presented in ref. 11.

Chlorobenzene, benzaldehyde and acetone were dried and distilled under nitrogen. All other reagents and solvents were commercially available and used as received.

We synthesized (+)- and (−)-*endo*-norborn-5-ene-2-ol via enzymatic resolution of their racemic butyric acid esters using lipases from *Candida cylindracea* and *Pseudomonas* sp.[12]. The enantiomeric purity of the monomers defined by the enantiomeric excess ($ee=(R-S)/(R+S)$) is shown in *Table 1*. The acetate, butyrate and benzoate monomers were prepared via standard esterification reactions.

Ring-opening metathesis polymerization was carried out in chlorobenzene under nitrogen atmosphere in a glovebox using $\mathrm{Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2}$ as catalyst. The polymerization was stopped by quenching with benzaldehyde or acetone. Then the polymers were precipitated in a more than fivefold excess of methanol, washed and dried. If impurities (monomer, catalyst, etc.) were detected in the polymer, by means of i.r. or n.m.r. spectroscopy (Bruker model MSL 300) or by colour, the polymer was purified by another precipitation from CH_2Cl_2/MeOH.

Table 1 Specific rotations of the monomers

Monomer		$[\alpha]_D^{20}$ (deg)	Concentration (g/100 ml $CHCl_3$)	*ee* (%)
a	(−)-Acetate	−129.0	4.60	>95
b	(−)-Butyrate I	−111.72	1.00	>95
b′	(−)-Butyrate II	−75.53	2.10	61
c	(−)-Benzoate	−98.52	2.95	>95
d	(+)-Acetate	+94.98	1.65	72
e	(rac)-Acetate	−1.2	1.68	1

In aqueous ROMP first a mixture of $K_2[RuCl_5(H_2O)]$ and 7-oxanorbornene-2,3-dicarboxylic acid dimethyl ester (ca. 5 mol% of the norbornenyl ester) in ethanol/water (1:1) was used to make the active initiator complex under polymerization of the excess of the monomer. For details about the initiating system see ref. 13. After separation of the precipitated poly(7-oxanorbornene-2,3-dicarboxylic acid dimethyl ester), the chiral monomer was then added to the reaction solution. The polymer was separated by pouring the reaction mixture into methanol and dried *in vacuo* at room temperature for 12 h.

For the determination of the optical activity, 20–50 mg of the monomers or polymers were dissolved in 2 ml $CHCl_3$. The solutions were transferred into the glass cuvette of the polarimeter (a Jasco DIP-370 Digital-Polarimeter). The specific rotation $[\alpha]_D^{20}$ was measured at a wavelength of 589 nm using two different concentrations. The experimental data for the monomers are given in *Table 1*.

Gel permeation chromatography (g.p.c.) was carried out with tetrahydrofuran as the eluent using three PL columns (10 μm/10 000 Å, 5 μm/1000 Å and 5 μm/100 Å) and a Waters differential refractometer R 401 as the detector.

RESULTS AND DISCUSSION

According to the initiating system, some drastic differences in the polymer properties were observed (see *Table 2*).

The g.p.c. data show a lower average molar mass and a narrower distribution of molar mass for the molybdenum-catalysed polymers. The lower polydispersity index (*PDI*) values of these polymers is a result of the 'living polymerization' for which this system is known. In g.p.c. graphs often a second peak appears corresponding to a molar mass twice that associated with the main peak. This is due to an incomplete quenching reaction so that two polymer chains can combine. Such a bimodal molar-mass distribution was also observed by Feast *et al.*[14]. This also explains the comparatively high *PDI* values because they were calculated over the whole peak areas.

No drastic differences can be seen in infra-red spectra. Evaluation of *cis/trans* ratio from i.r. is difficult because

Table 2 Properties of the polymers

Polymer	Initiator[a]	$[\alpha]_D^{20}$ (deg)	Concentration (g/100 ml $CHCl_3$)	Mass (10^3 g mol^{-1})	*PDI*
Polymer **a**	I	+33.30	2.42	466	1.87
	II	+42.80	1.70	197	1.67
	III	+71.70	1.45	140	1.17
Polymer **b**	I	+38.20	1.10	698	2.50
	II	+54.54	1.28	224	3.40
Polymer **b′**	I	+22.65	1.80	981	1.62
	II	+27.40	2.11	208	1.46
Polymer **c**	II	+87.23	1.00	173	1.36
Polymer **d**	I	−16.00	1.90	805	1.78
	II	−23.71	1.25	57	1.50
Polymer **e**	I	+0.7	2.46	554	2.16
	II	+0.8	1.65	105	1.39

[a] Initiators: I, $K_2RuCl_5(H_2O)$, solvent EtOH/H_2O; II, $\mathrm{Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2}$, solvent chlorobenzene; III, $\mathrm{Mo(CH\text{-}t\text{-}Bu)(NAr)(OCMe(CF_3)_2)_2}$, solvent chlorobenzene; (NAr) = 2,6-diisopropylaniline

of different absorbance coefficients of *cis* and *trans* double bonds.

N.m.r. studies show that the molybdenum-catalysed polymers exhibit higher *cis* double-bond content compared to ruthenium-catalysed polymers (see *Figures 1–4* and *Table 3*). *Figures 1* and *2* show the ^{1}H spectra of (−)-*endo*-2-norbornene acetate (polymer **a**). In *Figure 2* an additional peak from poly(7-oxanorbornene-2,3-dicarboxylic acid dimethyl ester) appears at 3.7 ppm. Detailed ^{13}C n.m.r. studies (*Figures 3* and *4*) show that all molybdenum-catalysed polymers are atactic with respect to both *cis* and *trans* vinylene units. Ruthenium-catalysed polymers lean towards being tactic with *trans* vinylenes occurring more frequently in meso dyads (60%) and *cis* vinylenes occurring in racemic dyads to a higher extent[15,16]. These assignments follow from the work of Ivin, who has established that the multiplicity of vinylic signals can be related to tacticity. Thus, HH/HT/TT/TH signals may be identified via substituent shift parameters when one enantiomer of a 5-substituted norbornene is polymerized HH and TT signals are diagnostic of racemic (r) dyads and HT and TH signals of meso (m) dyads[10].

Table 3 Results of ^{13}C n.m.r. analysis

Polymer	Initiator^a	σ_c^{b}	$(\sigma_r)_c$^{c}	$(\sigma_m)_t$^{d}
Polymer **a**	I	0.22	0.70	0.60
Polymer **a**	II	0.34	0.60	0.60
Polymer **a**	III	0.62	0.75	0.75

[a] See *Table 2*
[b] Fraction of double bonds having *cis* configuration
[c] Fraction of racemic *cis* double bonds
[d] Fraction of meso *trans* double bonds

The specific rotation values $[\alpha]_D^{20}$ of the polymers are summarized in *Table 2*. The molybdenum-catalysed polymers show a higher specific rotation compared to ruthenium-catalysed polymers. This may be associated with the higher proportion of racemic *cis* connections. *Table 3* shows the results of ^{13}C n.m.r. analysis of polymer **a**. Alternatively, in the ruthenium-catalysed polymerizations, 7-oxanorbornene-2,3-dicarboxylic acid dimethyl ester from the initiator complex was copolymerized (2.7%, see *Figure 2* at 3.7 ppm), giving a product with a reduced content of chiral units.

The tendency for the increasing specific rotations of the polymers from acetate to butyrate to benzoate may be connected with the increasing group size: the small acetate group may not affect the orientation of the polymer chain to the extent that the butyrate group does. The benzoate group may even be steering as in the case of helical poly(triphenylmethyl methacrylate)[5]. There could therefore be a helical contribution to the total specific rotation. In the general case there are six possible dyad structures for a polymer formed from (−)-monomers. *Figure 5* displays one of the possible dyad structures, six dyads long, a calculated model (by Alchemy II molecular modelling software) of only head–tail/meso/*trans* connected poly((−)-*endo*-2-norbornene acetate). From n.m.r. studies this structure could be associated with the ruthenium-catalysed polymers. The view along the polymer chain shows a helical structure with four monomer units per 360°

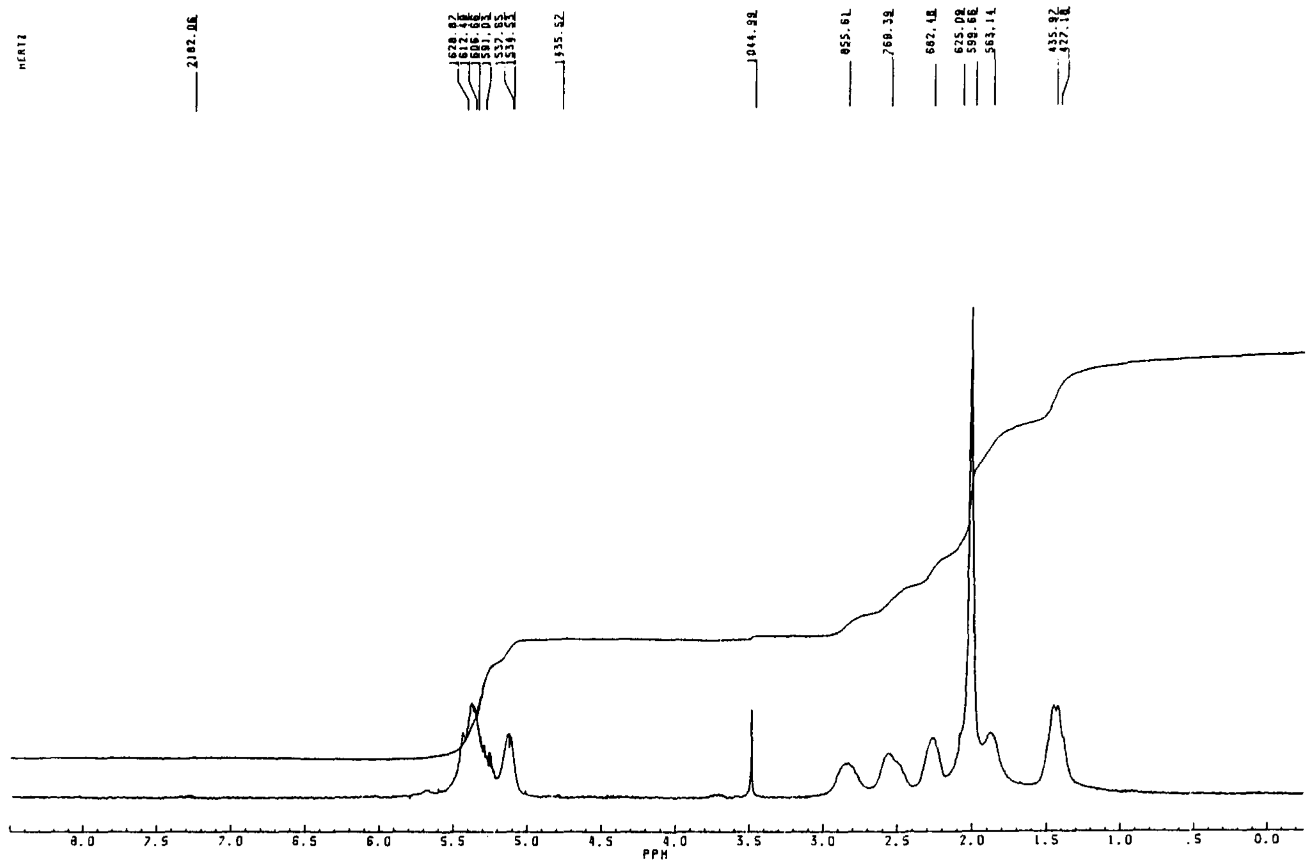

Figure 1 ^{1}H n.m.r. spectrum of the polymer from Mo-catalysed (−)-*endo*-2-norbornene acetate (polymer **a** II)

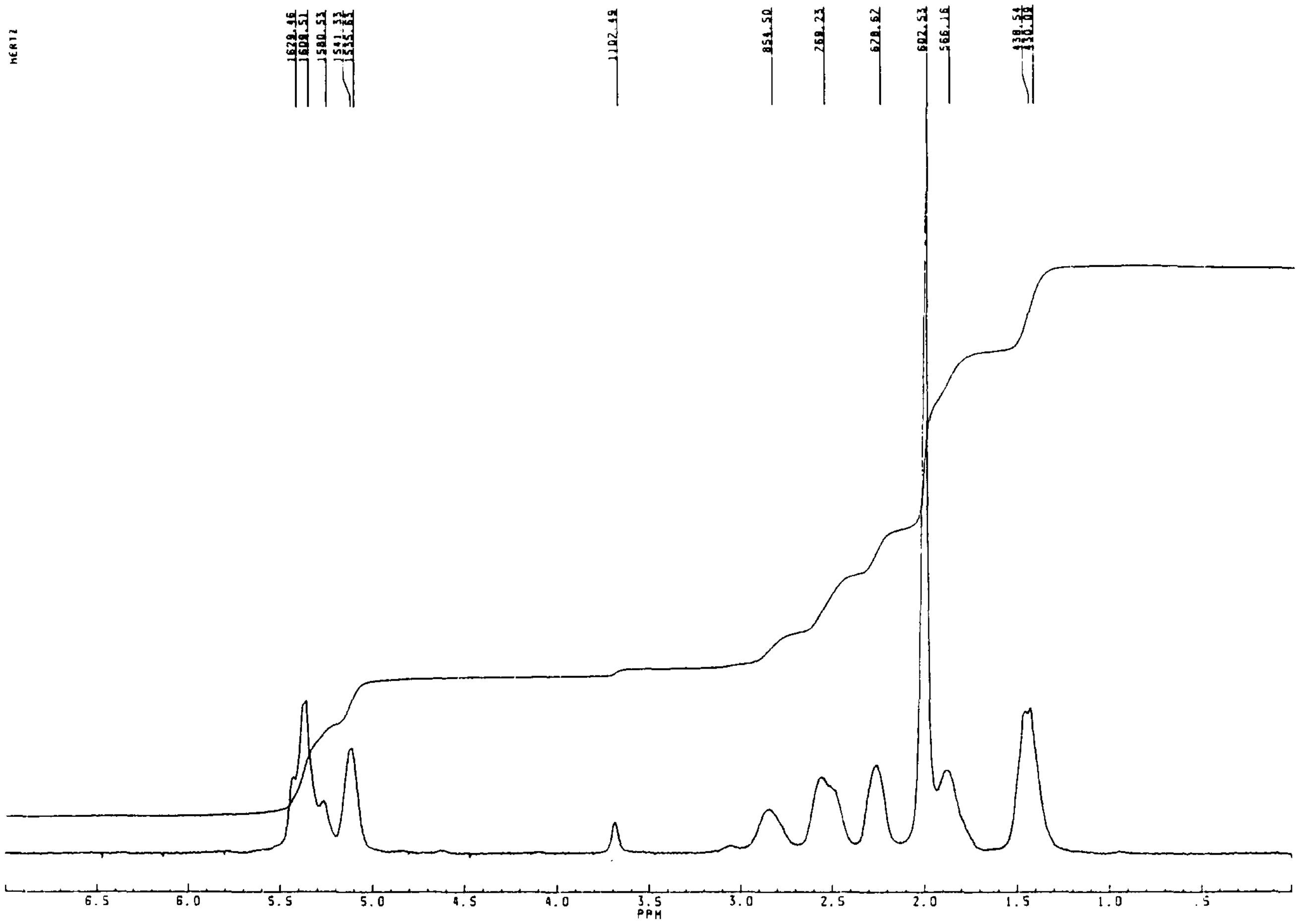

Figure 2 ^{1}H n.m.r. spectrum of the polymer from Ru-catalysed (−)-*endo*-2-norbornene acetate (polymer **a** I)

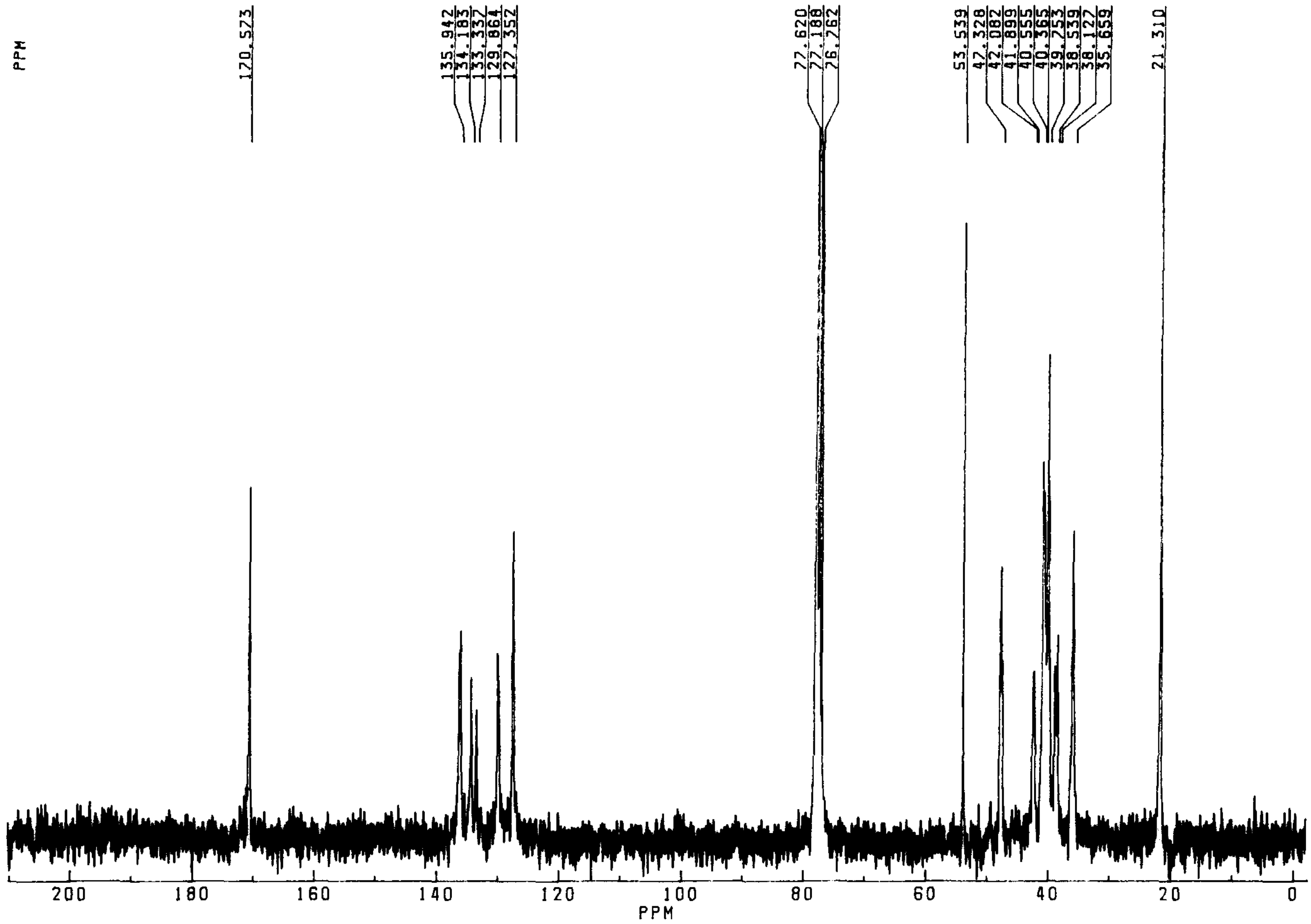

Figure 3 ^{13}C n.m.r. spectrum of the polymer from Mo-catalysed (−)-*endo*-2-norbornene acetate (polymer **a** II)

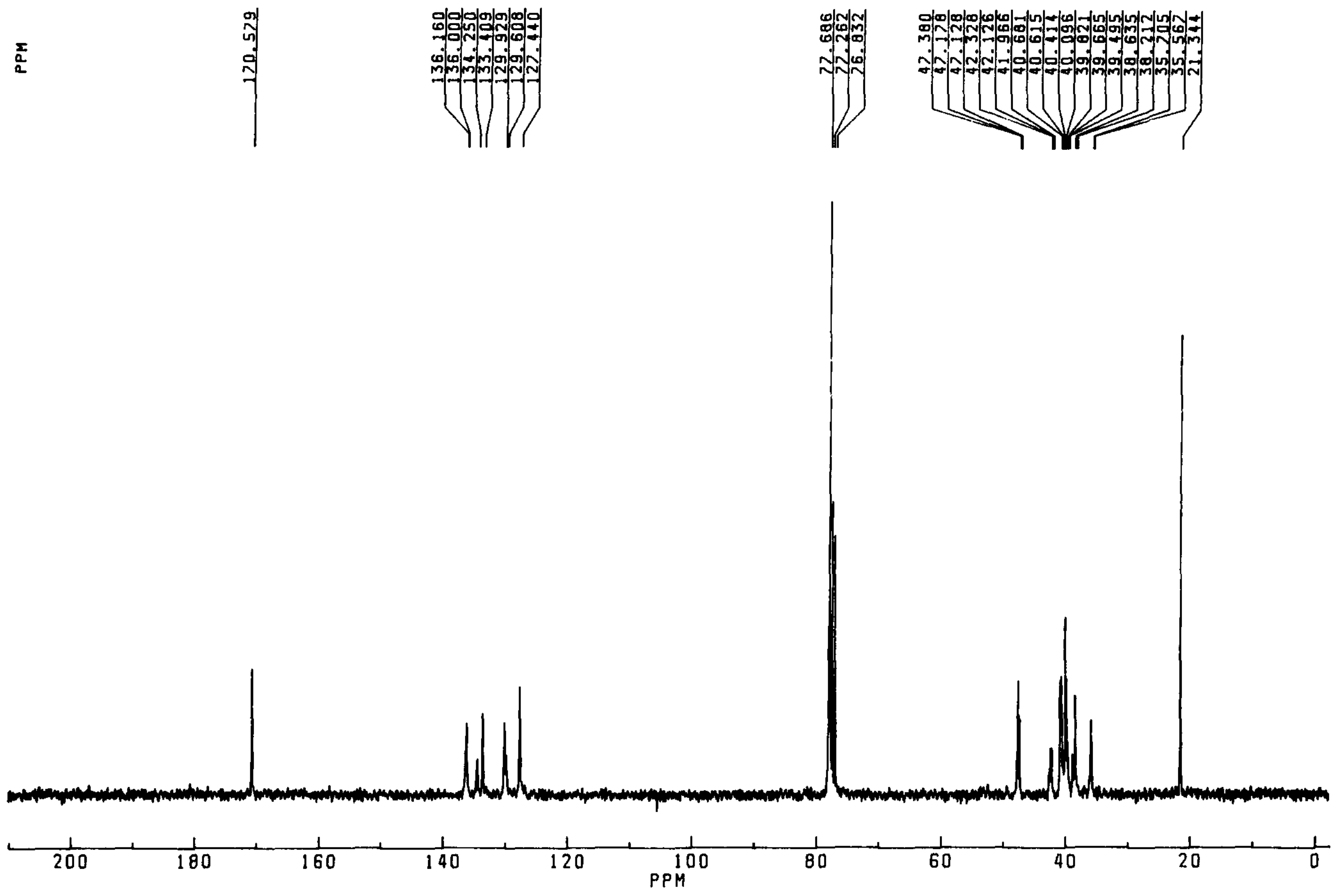

Figure 4 ^{13}C n.m.r. spectrum of the polymer from Ru-catalysed (−)-*endo*-2-norbornene acetate (polymer **a** I)

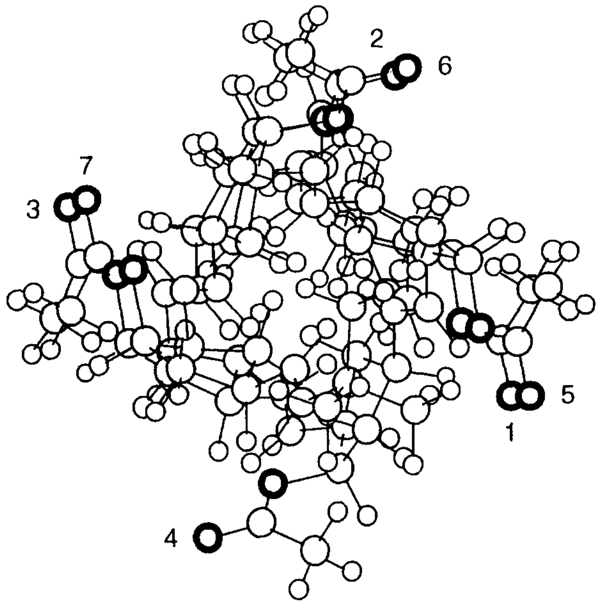

Figure 5 Alchemy II model of the head–tail/meso dyad/*trans* vinylene (HT/m/t) connected polymer **a**, viewed 3° off the polymer chain winding. The bold atoms are oxygens. The numbered ones are the oxygens of the carbonyl group of the acetate.

A structure fitting better to the molybdenum-catalysed polymers is shown in *Figure 6*. In this heptad the monomers are connected by head–head/racemic/*cis* vinylenes only. Again, the bold atoms are oxygens. The numbered ones are the oxygens of the carbonyl group of the acetate. The view along the chain shows no helicity.

Since the polymer with the highest content of this HH/r/c unit (polymer **a** III) exhibits the highest specific rotation within the series of polymers **a** but, according to our modelling studies, does not exist in a helical conformation, helicity cannot be the cause for optical activity, but must simply be a consequence of tacticity. At the moment detailed studies on the effect of various solvents and various catalysts on the tacticity of optically active polymers are in progress.

Previous experiments showed that these polymers can be copolymerized with styrene and divinylbenzene by standard techniques[17] to give insoluble materials for chiral stationary phases[18].

CONCLUSION

The ring-opening metathesis polymerization (ROMP) of chiral enantiomerically pure 2-substituted norbornenes carried out with $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}R)_2$ in chlorobenzene, where R = t-Bu or $CMe(CF_3)_2$, or $K_2[RuCl_5(H_2O)]$ in aqueous solvents leads to polymers that show optical activity.

The molybdenum-catalysed polymers show a higher specific rotation compared to ruthenium-catalysed polymers. On the one hand, this might be due to the higher amount of racemic *cis* connections in the polymer; on the other hand, ruthenium-catalysed polymers contain units stemming from 7-oxanorbornene-2,3-dicarboxylic acid dimethyl ester from the initiating complex, which have a dilution effect. The molybdenum-catalysed polymers have a lower average molar mass and a

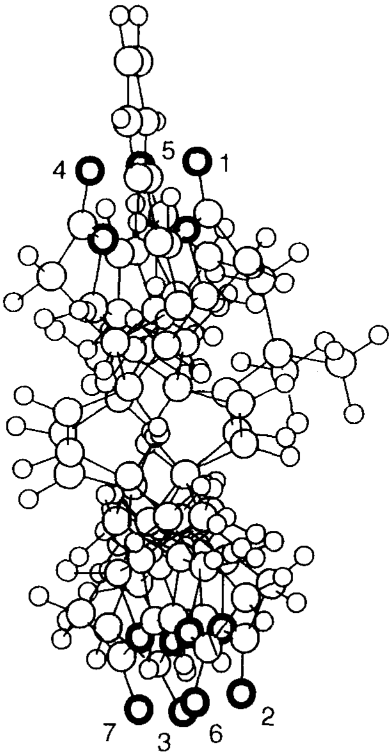

Figure 6 Alchemy II model of the head–head/racemic dyad/*cis* vinylene (HH/r/c) connected polymer **a**, viewed 3° off the polymer chain

narrower distribution. N.m.r. studies show that the molybdenum-catalysed polymers (in chlorobenzene as the solvent) are connected *cis*-wise to about 30% and are atactic with respect to both *cis* and *trans* vinylene units, whereas the ruthenium-catalysed polymers are *cis* connected to only 20% but lean towards being tactic with *trans* vinylenes occurring more in meso dyads (60%) and *cis* vinylenes occurring in racemic dyads to a higher extent.

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REFERENCES

1 Consiglio, G. and Waymouth, R. M. *Chem. Rev.* 1989, **89**, 257
2 Wulff, G. and Wu, Y. *Makromol. Chem.* 1990, **191**, 2993
3 Wulff, G. *Chem. Tech.* 1991, **21** (6), 364
4 Moore, J. S., Gorman, C. B. and Grubbs, R. H. *J. Am. Chem. Soc.* 1991, **113**, 1704
5 Liu, J.-H., Kuo, J.-C. and Fang, M. C. *J. Appl. Polym. Sci.* 1992, **45**, 1587
6 Okamoto, Y. and Hatada, K. in 'Chromatographic Chiral Separations' (Eds. M. Zief and L. J. Crane), Marcel Dekker, New York, 1988, pp. 199–218
7 Vogl, O., Jaycox, G. D., Xi, F. and Hatada, K. *Polym. Prepr.* 1989, **30** (2), 435
8 Lifson, S., Felder, C. E. and Green, M. M. *Macromolecules* 1992, **25**, 4142
9 Deming, T. J. and Novak, B. M. *Polym. Prepr.* 1991, **32**, 455
10 Hamilton, J. G., Ivin, K. J. and Rooney, J. J. *J. Mol. Catal.* 1985, **28**, 255
11 Yuvev, Yu. K. and Zefirov, N. S. *J. Gen. Chem. USSR* (Engl. Transl.) 1963, **33**, 795
12 Oberhauser, Th., Bodenteich, M., Faber, K., Penn, G. and Griengl, H. *Tetrahedron* 1987, **43** (17), 3931
13 Zenkl, E. and Stelzer, F. *J. Mol. Catal.* 1992, **76**, 1
14 Feast, W. J., Gibson, V. C., Khosravi, E., Marshall, E. L. and Mitchell, J. P. *Polym. Commun.* 1992, **33**, 872
15 Ivin, K. J. in 'Olefin Metathesis and Polymerization Catalysis', (Ed. Y. Imamoglu), Kluwer Academic, The Netherlands, 1990, pp. 187–207
16 Ivin, K. J., Lam, L. M. and Rooney, J. J. *Makromol. Chem.* in press
17 Braun, D., Cherdron, H. and Kern, W. 'Praktikum der makromolekularen organischen Chemie', 2nd Edn., Hüthig Verlag, Heidelberg, 1971
18 Steinhäusler, T., Diploma Thesis, TU Graz, 1992