FULL PAPER

Optically Active, Isotactic Homopolymers of α-Olefins with Main-Chain Chirality and the First Preparation of Optically Active C_3-Symmetrical Polymers

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Abstract: Enantiomerically pure or enriched isotactic poly(methyl methacrylates) of varying molar masses and carrying one reactive amino end group have been prepared from the corresponding poly(trityl methacrylates) and poly(diphenyl-2-pyridylmethyl methacrylates). It was of special interest to investigate the dependence of their chiroptical properties with respect to the chain length. Only at a rather high P_n ($P_n > 300$), the optical activity becomes negligible, and the polymers can be called cryptochiral. Coupling of three such chains to 1,3,5-benzenetricarbonyl chloride results in three-armed star polymers with C_3 symmetry. Their optical rotation is measured as such in solution and after transforming the polymers with achiral syndiotactic poly(methyl methacrylates) into helical stereocomplexes. The polymers, especially the helical stereocomplexes, have remarkably high optical rotations. These compounds are the first optically active polymers with C_3 symmetry.

Keywords: chirality · optical activity · polymers · stereocomplexes · C_3 symmetry

Introduction

In recent years, optically active polymers with chirality in the main chain (main-chain chiral polymers) have attracted considerable interest. In this respect polymers from 1-substituted or nonsymmetric 1,1-disubstituted olefins (technically the most important polymers) are especially interesting.[1–3] Whereas many examples are known for chiral copolymers[1, 4] and helical polymers with atropisomeric structures,[3] there are only a few reports on the structural chirality of homopolymers. One route to optically active homopolymers with main-chain chirality starts with the preparation of a heterotactic polymeric chain, in which dyads (introduced by chiral template molecules) of defined absolute configuration ((S,S) or (R,R)) are alternating with atactic sequences of the same monomeric unit.[5] In such a case, optical activity is independent of the chain length.

Isotactic homopolymers represent an especially interesting case since they are usually regarded as being achiral.[6, 7] An isotactic chain with an even number of monomeric units is represented as a model of an ideal chain (**1**). If chain ends are identical (that is $R^1-CH_2 = R^2$), **1** possesses a mirror plane

1   **2**

3
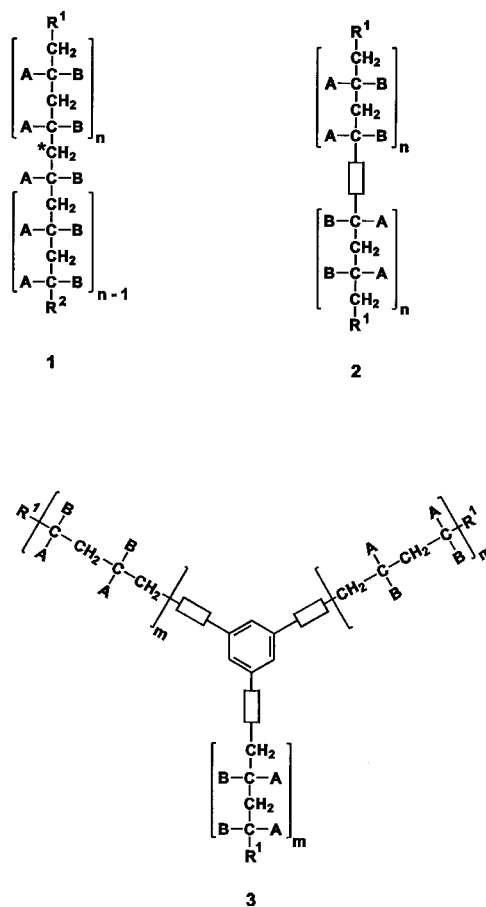
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(crossing the marked *C carbon in **1**) and is therefore a meso compound. The same holds true if there is an odd number of monomeric units.

If R^1-CH_2 and R^2 are different, the chain becomes chiral. It is usually assumed that, with long polymeric chains, the difference of the end groups can be neglected so that, in the case of a single enantiomer, no chiroptical properties can be measured.[6, 7] Similar to analogous cases,[8] such behavior may be called cryptochiral. As a result of new preparative possibilities, it is now possible to prepare single enantiomers of isotactic chains of defined chain length. This should allow the extent of cryptochirality to be investigated, and answer the question of how long the chains must be until the optical activity disappears and the polymers become cryptochiral.

Anionic polymerization of trityl methacrylate in the presence of chiral catalysts, first introduced by Okamoto et al,[3, 9] gives highly isotactic polymers that exhibit strong optical activity and that are present as stable, one-handed (atropisomeric) helices. After replacement of the trityl group by the much smaller methyl group, the polymer adopts a random-coil conformation, and the optical activity becomes very small. However, investigations of the oligomers obtained in this polymerization reaction show[10–13] that the stereogenic centers in the main chain are formed with high asymmetric induction and with uniform absolute configuration. A systematic investigation of oligomers up to the decamer carried out by Okamoto et al.[13] showed that, especially at higher P_n, the chains were completely isotactic (except the termination end) and represented a single enantiomer. Anionic polymerization offers therefore the possibility for the preparation of defined single enantiomers of isotactic poly(methyl methacrylate) (PMMA) with much higher P_n.
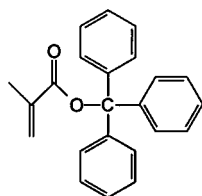
In two short communications, we have recently reported that chiroptical properties in isotactic PMMA can be measured up to a P_n of 300 in the case of poly(methyl methacrylates) with different chain ends.[14, 15] If two enantiomerically pure or enriched isotactic poly(methyl methacrylates) carrying one reactive amino end group are coupled to a linker, such as a diacid dichloride, polymers of type **2** are obtained.[15] The resulting elongated polymers have an inverse-diblock-isotactic structure with identical chain ends and, consequently, C_2 symmetry. These polymers possess a surprisingly high optical activity, especially if they are forced into a helical conformation. It can be foreseen that only at higher molar masses (M_n = above 100000) the polymers will no longer show any optical activity and will finally become cryptochiral.
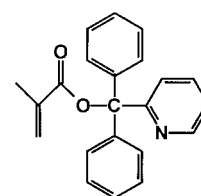
In this paper, the preparation of optically active, isotactic PMMA with varying chain length and different chain ends will be discussed in detail, and the preparation of optically active C_3-symmetrical polymers **3** will be described. To our knowledge, C_3-symmetrical polymers have not been described before.[16] Low molecular weight compounds with C_3 symmetry have found increasing interest in recent times, and an up-to-date account of this field has recently been given in a review by Moberg.[17]
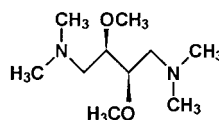
Results and Discussion

The preparation of reactive, isotactic poly(methyl methacrylates): Initial experiments for preparing enantiomerically pure or enriched isotactic poly(methyl methacrylates) (PMMA) used the anionic polymerization of trityl methacrylate in the presence of chiral catalysts [(+)- or (−)-2,3-dimethoxy-1,4-bis(dimethylamino)butane; ((+)- or (−)-DDB)].[14] Typical initiators were diphenylmethyllithium or atactic polystyryllithium. The trityl groups were subsequently replaced by methyl groups, thus furnishing optically active isotactic PMMA. PMMA's optical activity increased as the difference between the end groups R^1CH_2 and R^2 became more
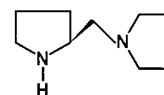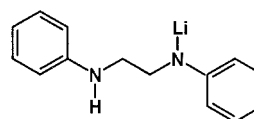
Abstract in German: *Es wurden enantiomerenreine oder angereicherte isotaktische Poly(methyl methacrylate) mit variierender Molmasse hergestellt. Als Ausgangsprodukt benutzte man die entsprechenden Poly(trityl methacrylate) und Poly-(diphenyl-2-pyridylmethyl methacrylate), die jeweils eine reaktive Aminoendgruppe trugen. Von besonderem Interesse war die Abhängigkeit der chiroptischen Eigenschaften von der Kettenlänge. Erst bei recht hohen P_n ($P_n > 300$) wird die optische Drehung vernachlässigbar und die Polymere können als cryptochiral angesehen werden. Werden drei solcher Ketten an 1,3,5-Benzoltricarbonylchlorid gekoppelt, erhält man dreiarmige Sternpolymere mit C_3-Symmetrie. Deren optische Drehung wird sowohl in Lösung direkt vermessen als auch nach Überführung mit achiralem syndiotaktischen Poly(methyl methacrylat) in helikale Stereokomplexe. Diese Sternpolymere, vor allem die helikalen Stereokomplexe, besitzen bemerkenswert hohe optische Drehungen. Es handelt sich hierbei um die ersten optisch aktiven Polymere mit C_3-Symmetrie.*

Trityl methacrylate

Diphenyl-2-pyridylmethyl methacrylate

(+)− DDB

(+)− PMP

N,N'- Diphenylethylendiamine monolithium amide

pronounced, but the optical activity decreased with higher chain length. Unfortunately, this method did not allow the preparation of polymers with appreciably higher molar masses than $P_n = 83$, which would allow more detailed studies of the dependence of the optical activity on molar mass. Furthermore, the preparation of polymers of type **2** and type **3** requires an isotactic PMMA with one reactive end group.

Okamoto's group[18] polymerized trityl methacrylate anionically with the mono-lithium amide of N,N'-diphenylethylenediamine as initiator in the presence of (+)- or (−)-DDB as chiral catalysts. This method has been used for the preparation of macromonomers of poly(trityl methacrylate). We have used the same method and replaced the trityl group afterwards by a methyl group. By varying the monomer–initiator ratio and working under carefully controlled conditions, degrees of polymerization P_n between 27 and 109 could be achieved (Table 1). As expected, the poly(trityl methacrylates) showed high optical rotations, $[\alpha]_{365}^{20}$ between +1275°

Table 1. Preparation and properties of poly(trityl methacrylate) **PI** and poly(methyl methacrylate) **PIII**.[a]

Prepared polymer **PI**	$[\alpha]_{365}^{20}$[b] [°]	Prepared PMMA	M_n[c]	$[\alpha]_{546}^{20}$[d] [°]	$[\alpha]_{546}^{20}$[e] [°] complex
PI 1	+1275	**PIII 1**	2700	− 0.9	− 1.9
PI 2	+1375	**PIII 2**	3950	− 0.8	− 0.6
PI 3	+1398	**PIII 3**	4400	− 0.6	− 0.6
PI 4	+1403	**PIII 4**	4500	− 0.7	− 0.6
PI 5	+1408	**PIII 5**	5400	− 0.4	− 0.2
PI 6	+1426	**PIII 6**	5850	− 0.4	+ 0.2
PI 7	+1411	**PIII 7**	7450	− 0.2	+ 0.3
PI 8	+1499	**PIII 8**	10900	− 0.4	+ 0.2
PI 9[b]	−1399	**PIII 9**	4500	+ 0.2	+ 0.9

[a] Anionic polymerization of trityl methacrylate in toluene (1 g/20 mL) with the monolithium amide of N,N'-diphenylethylenediamine complexed with 1.2 equivalent of (S,S)-1,4-bis(dimethylamino)-2,3-dimethoxybutane ((+)-DDB). In the case of **PI 9**, (+)-DDB is replaced by (−)-DDB in such a way that the enantiomers with opposite configuration and optical rotation are obtained. Molar ratios of initiator:monomer between 1:12 and 1:50 (Table 4). [b] Specific optical rotation in THF, $c = 0.5$. [c] Determined by analytical GPC by comparison with polystyrene standards, values are rounded. [d] Specific optical rotation in benzene, $c = 0.3$. [e] Specific optical rotation after preparation of the corresponding stereocomplexes with syndiotactic poly(methyl methacrylate) in benzene, $c = 0.3$ (calculated for the **PIII** content).

and +1499°, when prepared with (+)-DDB; after using the enantiomer (−)-DDB, the opposite sign of rotation $[\alpha]_{365}^{20} = -1399°$ was observed. The resulting PMMA showed small but significant optical rotations between − 0.9° and − 0.2° depending on the chain length.

It is known from Okamoto's work[3, 19] that diphenyl-2-pyridylmethyl methacrylate (D2PyMA) can be polymerized in a more controlled manner than trityl methacrylate and provides polymers with higher stereoregularity and defined predetermined molar masses. Therefore D2PyMA was polymerized with (N,N'-diphenylethylenediamine) monolithium as initiator and (S)-1-(2-pyrrolidinylmethyl)pyrrolidine ((+)-PMP) as the chiral ligand.[19] Again the monomer–initiator ratio was varied, and poly(diphenyl-2-pyridylmethyl methacrylate) **PII** was obtained with P_n between 30 and 260, thus allowing a very large range of molar masses to be reached

(Table 2). The optical rotations were even somewhat higher as with poly(trityl methacrylate) **PI**. Transformation of these polymers **PII 1–10** by transesterification with methanolic HCl and treatment with diazomethane (to ensure complete esterification) yielded the corresponding PMMAs **PIV 1–10**

Table 2. Preparation and properties of poly(diphenyl-2-pyridylmethyl methacrylate) (PD-2-PyMA) **PII** and poly(methyl methacrylate) **PIV** prepared from **PII**.

Prepared polymer	$[\alpha]_{365}^{20}$[b]	Prepared PMMA	M_n[c]	$[\alpha]_{546}^{20}$[d]	$[\alpha]_{546}^{20}$[e] complex	$[\alpha]_{365}^{20}$[a] complex
PII 1	+1318	**PIV 1**	3050	− 3.0	− 5.1	− 20.5
PII 2	+1425	**PIV 2**	3900	− 2.2	− 4.1	− 14.5
PII 3	+1495	**PIV 3**	4500	− 1.7	− 1.9	− 10.3
PII 4	+1485	**PIV 4**	4600	− 1.4	− 1.8	− 10.6
PII 5	+1512	**PIV 5**	6000	− 1.4	− 0.2	− 8.7
PII 6	+1532	**PIV 6**	7850	− 1.3	+ 1.4	− 5.9
PII 7	+1507	**PIV 7**	9600	− 0.9	+ 1.6	− 3.4
PII 8	+1518	**PIV 8**	12050	− 1.2	+ 1.0	− 1.2
PII 9	+1490	**PIV 9**	24800	− 0.4	+ 0.4	− 0.3
PII 10	+1465	**PIV 10**	26050	− 0.5	+ 0.9	− 0.1

[a] Specific optical rotation after preparation of the corresponding stereocomplexes with the coblock polymer **PV** containing a syndiotactic PMMA block and a syndiotactic poly(benzyl methacrylate) in benzene, $c = 0.3$ (calculated for the **PIV** content). [b]–[e] See Table 1.

(Table 2). Table 2 and Figure 1 show that the resulting PMMAs possess higher optical rotation than PMMA **PIII** obtained from poly(trityl methacrylate) **PI**. Optical rotations $[\alpha]_{546}^{20}$ ranged from 3.0° to 0.5° depending on the molecular weights M_n (3050 to 26050). Though these optical rotations are quite significant, the values cannot be interpreted quantitatively since the error in the determinations (±0.2–0.3°) is too large.
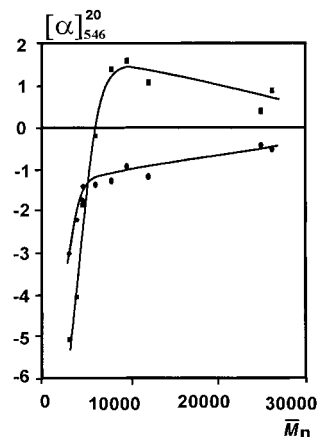

Figure 1. Dependence of optical activity of polymers on the molecular weight. Lower curve: isotactic polymers PMMA **PIV 1–10** prepared by anionic polymerization of diphenyl-2-pyridylmethyl methacrylate with (N,N'-diphenylethylenediamine) monolithium as initiator and (S)-1-(2-pyrrolidinylmethyl)pyrrolidine as the chiral ligand. The polymers obtained **PII 1–10** were transformed to the methylesters **PIV 1–10**. Upper curve: optical rotation of the stereocomplexes of **PIV 1–10** with a block copolymer **PV** of syndiotactic PMMA and syndiotactic poly(benzyl methacrylate).

Investigations on the chiroptical properties of the isotactic PMMA PIII and PIV: PMMA **PIII** and **PIV** exist mainly in a random coil conformation, and their optical activity originates

therefore from the configuration of the main chain. In addition, we have attempted to investigate the effect of the conformation on the optical activity. Isotactic PMMA can undergo a transition to helical conformations; in the case of identical chain ends ($R^1CH_2 = R^2$), that is a *meso* form, the ($+$) and the ($-$) helices should be formed with equal probability. However, if helix formation from one chain end is favored owing to differing chain ends, then diastereomeric ($+$) and ($-$) helices should be formed from an enantiomerically pure chain, and one screw sense of the helix should be preferred.

In order to transform the isotactic PMMA chains into helices to an appreciable extent, stereocomplexes with achiral syndiotactic PMMA chains were prepared. Stereocomplexes of optically inactive isotactic PMMA with syndiotactic PMMA have been carefully investigated before by other groups.[20–22] It is assumed that the isotactic PMMA chain is present as a tightly folded inner helix surrounded by a 9/1 double helix composed of syndiotactic PMMA. We have applied stereocomplexing for the first time to chiral polymers, and we have thus been able to show that the optical activity of the isotactic PMMAs can be enhanced by a factor of 2–5.[14, 15] Complexes were prepared in benzene solution, and in equilibrium around 40% of the isotactic chains of PMMA were complexed. Usually a syndiotactic PMMA of $M_n \approx 35\,000$ was used for making the stereocomplexes. In the case of PMMA **P IV**, some had high molar masses, and the resulting stereocomplexes became insoluble. In order to measure the whole series **P IV 1–10** under identical conditions, we undertook a careful investigation of different syndiotactic PMMAs for use in stereocomplexing.

Since it is known that the ester group of syndiotactic PMMA in the stereocomplex is oriented to the outer side of the helix, the structure of the ester group is less important for stereocomplexing.[21, 23] We have therefore prepared syndiotactic poly(benzyl methacrylate) which is much more soluble. However, its ability to form stereocomplexes was less pronounced, and the optical activities of the stereocomplexes were low compared to those of syndiotactic PMMA. The application of a block copolymer of syndiotactic PMMA and syndiotactic poly(benzyl methacrylate) was more successful. The copolymer was prepared by anionic polymerization of methyl methacrylate in toluene with the initiator *tert*-butyllithium/triethylaluminium, a method used for the preparation of syndiotactic PMMA.[24] The living system was subsequently elongated by a block of poly(benzyl methacrylate). The resulting block copolymer **P V** contained a PMMA block of $P_n \approx 144$ with around 87% of syndiotactic groups and a poly-(benzyl methacrylate) block of $P_n \approx 76$. This block copolymer **P V** was used for stereocomplexing **P IV 1–10**. The optical rotations obtained for the same isotactic PMMA with syndiotactic PMMA ($P_n = 350$) or the block copolymer **P V** were very similar, but the latter allowed soluble stereocomplexes of even high molecular weight isotactic PMMA to be prepared.

Table 1 shows that the optical rotation is enhanced by a factor of 2 for **P III 1**; at higher molecular weight this factor becomes less, and at higher molar masses, the sign of the optical rotation changes upon complexation. A similar

tendency is seen in Table 2 and Figure 1 for PMMA **P IV**. Here, the optical rotations ($[\alpha]_{546}^{20}$) are higher, but, again at higher molar masses, the optical rotation changes its sign. Interestingly, optical rotations measured at 365 nm show much higher absolute values as expected, but no change of the sign is observed up to M_n 26050. This behavior might be due to a Cotton effect. Therefore the ORD (optical rotatory dispersion) curves of **P IV 1**, **P IV 3**, and **P IV 7** were measured. Figure 2 shows that all three ORD curves possess principally the same form. The opposite sign of the optical rotation at higher molar masses does not indicate a different structure (for example, helicity) of the stereocomplexes. At a higher wavelength (546 nm), a positive optical rotation is observed for long chain polymers as can be seen from the curve of **P IV 7** in Figure 2. At the same time, the curves become more flat.
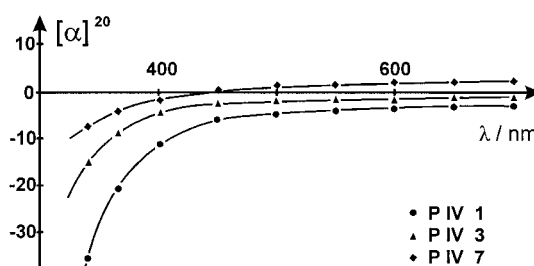
Figure 2. ORD curves of the stereocomplexes of **P IV 1**, **P IV 3**, and **P IV 7** with **P V**.

From these data, it is apparent that enantiomerically pure or enriched, isotactic PMMA with different chain ends shows chiroptical properties up to a P_n of 260 and probably even at higher molar masses. This was observed even in the case of PMMA **P IV**, where the difference between the end groups is much less pronounced than in earlier examples.[14]

If the polymer chain becomes much longer, the difference between the end groups is no longer reflected in the chiroptical properties, which become too small to be measured. The polymers are still chiral, but for practical reasons the chiroptical properties cannot be measured. As pointed out in the introduction, such behavior can be called cryptochiral. The chain length at which chirality turns into cryptochirality is much longer than was expected previously. In our case of single enantiomers of PMMA, this molar mass is certainly higher than M_n 30000.

It has been shown that stereocomplexing isotactic PMMA provides a good method for transforming the PMMA into a helical conformation and thus, in the case of chiral PMMA, the method allows the optical rotation to be enhanced considerably.[14] Comparison of the optical rotations of PMMA of various chain length with the optical rotations of their stereocomplexes shows that this dependence is not a simple one (Figure 1 and Table 1 and Table 2). The explanation for this complicated behavior is the influence of different and partly opposing effects.

For structural reasons, the influence of the chirality responsible for optical rotation should diminish with the length of the chain. Actually, only the first stereogenic centers at both chain ends contribute significantly to the optical rotation. On further elongation of the chain this effect is

diluted. The stereocomplexes show a Cotton effect that is not observed in PMMA itself (Figure 2). There is a third influence on the optical rotation in relation to the chain length. The extent of stereocomplexing between an isotactic chain and a syndiotactic one depends on the chain length of both polymers. If the chain length of the syndiotactic part is kept constant as in our case, complexing will be stronger with higher molar masses of the isotactic part. This means, that at higher molar masses of the isotactic chain, the percentage of helices becomes larger. This is also the reason for the lower solubility of stereocomplexes of higher molar masses. In spite of these complications, stereocomplexing is a good method for enhancing the chiroptical properties of the main chain chiral PMMAs. In the case of polymers of type **2**, an enhancement of optical rotation by a factor of 7–8 is observed.[15]

The preparation of a star-shaped C_3-symmetrical PMMA: As has been shown, isotactic poly(methyl methacrylates) **P III** and **P IV** with high enantiomeric purity and varying molar masses can be obtained. These polymers still contain a reactive secondary amino group (from the initiator molecule), which is capable of undergoing a coupling reaction. Polymers **P III** can indeed be coupled to adipoyl chloride in dichloromethane in the presence of triethylamine to give polymers of type **2**, as was described earlier.[15] In a similar fashion, polymers **P III** can be coupled to a trifunctional carboxylic acid derivative yielding C_3-symmetrical star-shaped polymers **P VI**. Achiral three-arm star poly(methyl methacrylate) of similar structure with syndiotactic PMMA arms has been recently prepared by Hatada's group.[24]

In this investigation, polymers **P III** have been used for coupling, since they can be prepared much easier than PMMA **P IV**. Thus, 1,3,5-benzenetricarbonyl chloride is reacted with some excess of polymers **P III** in methylene chloride in the presence of triethylamine (Scheme 1). The reaction could easily be followed by GPC (gel permeation chromatography, Figure 3a) and it proceeds quite slowly. After four days (Figure 3), three GPC peaks are observed. The first peak contains starting materials together with mono-coupling product, a shoulder represents the di-coupling product, and the main peak contains the desired tri-coupling product. After five days the reaction is stopped, and after several reprecipitations the pure polymers **P VI** could be obtained in yields of about 25%. According to GPC, molar masses were around three times greater than those for the starting polymer (Table 3). Figure 3b shows that precipitation yielded a product with narrow peak width in GPC. Polydispersities were around 1.15–1.17 and thus very similar to those of the starting compounds (1.12–1.16). This definitely shows that the coupling reaction was successful, and that polymers of type **3** with C_3 symmetry have been prepared.

The chiroptical properties of the newly prepared C_3-symmetrical polymers are particularly interesting. A comparison of the specific rotations of the starting polymers **P III** with those of the C_3-symmetrical polymers **P VI** shows that the optical rotations of **P VI** are of the same order of magnitude as the starting polymers **P III** (Table 1 and 3).

Strikingly, higher optical rotations are observed for stereocomplexes between polymer **P VI** and achiral syndiotactic
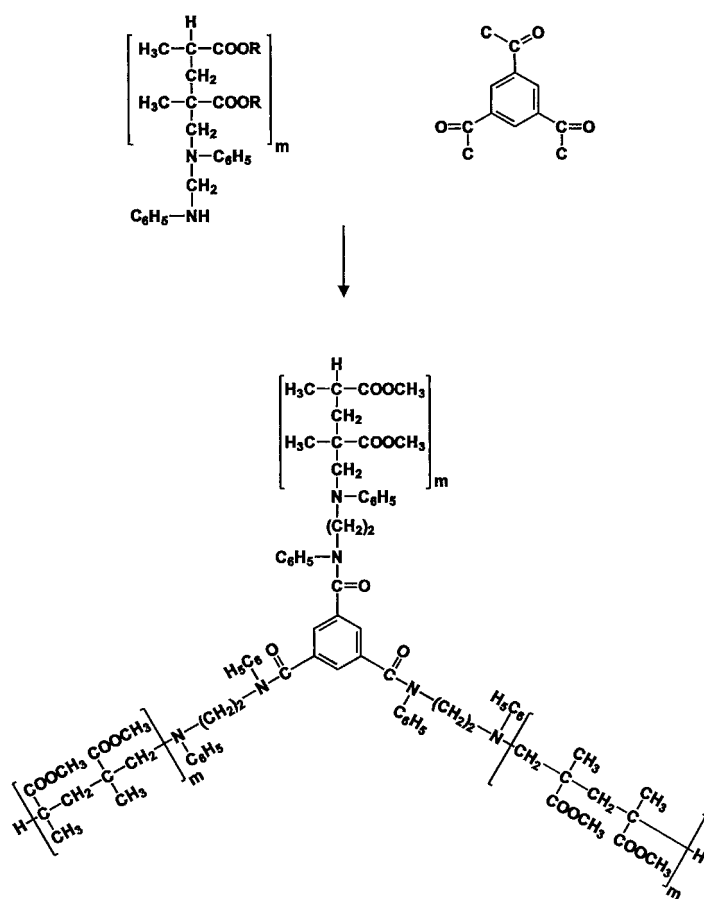
Scheme 1.
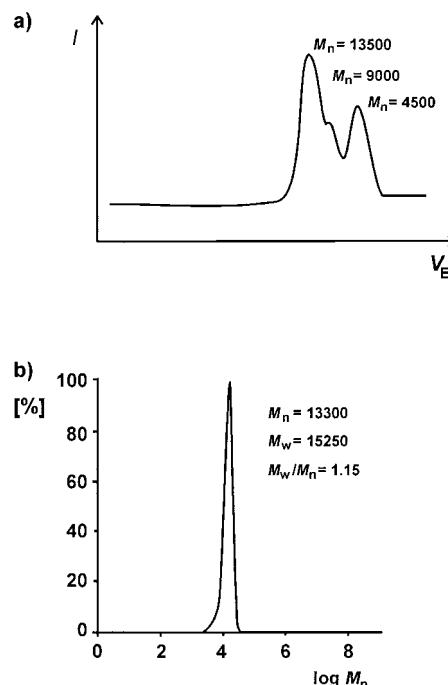
Figure 3. a) GPC analysis of the reaction mixture during preparation of **P VI 4** (after four days reaction time). The peak at $M_n \approx 4500$ contains starting material and mono-coupling product, the shoulder with $M_n \approx 9000$ the di-coupling product, and the main peak with $M_n \approx 13500$ contains the tri-coupling product. V_E = Elution volume. b) Molecular weight distribution from the purified **P VI 4** obtained by GPC calibration.

Table 3. Preparation and properties of three-armed star-shaped poly(methyl methacrylates).[a]

Polymer	Starting polymers				Three-armed poly(methyl methacrylates)					
	M_n	M_w/M_n	$[\alpha]_{546}^{20}$[b] complex		Polymer	M_n	M_w	M_w/M_n	$[\alpha]_{546}^{20}$[c]	$[\alpha]_{546}^{20}$[b] complex
P III 2	3 950	1.15	− 0.6		**P VI 2**	11 900	14 000	1.17	− 0.8	+ 3.9
P III 4	4 500	1.13	− 0.6		**P VI 4**	13 600	15 600	1.15	− 0.7	+ 3.6
P III 9[d]	4 500	1.10	+ 0.9		**P VI 9**[d]	13 300	15 200	1.15	+ 0.7	− 4.1

[a] Coupling of poly(methyl methacrylates) **P III** with benzenetricarbonyl chloride gives the three-armed polymers **P VI** with C_3 symmetry. M_n and M_w are determined by analytical GPC by comparison with polystyrene standards (Table 1). [b] Specific optical rotation after preparation of the corresponding stereocomplexes with syndiotactic poly(methyl methacrylates) in benzene, $c = 0.3$ (calculated for the **P III** or **P VI** content). [c] Specific optical rotation in benzene, $c = 0.3$. [d] This PMMA **P III 9** has been prepared with (−)-DDB, the optical antipode of the catalyst (+)-DDB, in the case of **P III 2** and **P III 4**.

PMMAs (similar to those already described for polymers **P III**). On stereocomplexing, absolute values increase by a factor of 5, but optical rotations have an opposite sign. As already pointed out, changes in optical rotation on stereocomplex formation show a rather complicated dependence on chain length.

The reason for the relatively high optical rotations of the stereocomplexes of C_3-symmetrical polymers **P VI** (compared to the enantiomerically pure or enriched PMMAs with different chain ends) can be explained as follows. In an isotactic chain with identical chain ends, both chain ends possess opposite absolute configuration ((R) and (S)). Therefore, on each side a helicity of opposite sign will be energetically more stable and will consequently be formed, resulting in no prevailing helicity. Enantiomerically pure isotactic chains with different chain ends show an excess of one helical screw sense, since the formation of the helix from both sides occurs with different probability and at a different rate so that one screw sense dominates.

In a C_3-symmetrical star-shaped polymer **P VI**, all three chains will adopt the same helicity sense. In all three outer chain ends, the chain starts with an identical absolute configuration. Thus the same screw sense of the helicity is expected to originate from all three chain ends of **P VI**. In the case of the stereocomplexes of **P VI**, we have therefore three identical chains attached to a benzene ring which all have the same absolute configuration and which all have the same preferred conformation with a helix of one screw sense (**4**). To the best of our knowledge, this is the first example of an optically active polymer having C_3 symmetry.

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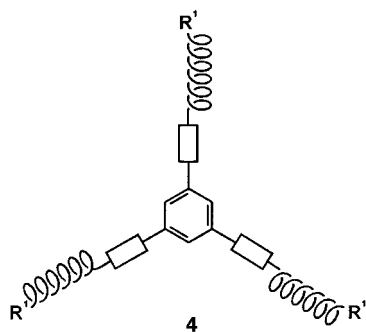
Experimental Section

General methods: Elemental analyses were performed in the microanalytical laboratories of the Faculty of Natural Sciences of the Heinrich-Heine-University in Düsseldorf. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer. Optical rotations and ORD were measured with a Perkin-Elmer 241 MC polarimeter (accuracy ± 0.002°). In the case of low optical rotations, the Polar Monitor from IBZ Meßtechnik, Hannover, was used. Using this instrument, measurement was made by the Faraday compensation technique (accuracy ± 0.0005°). This resulted in an average error of ± 0.2° for $[\alpha]$.

Materials: Toluene for anionic polymerizations was carefully dried and freshly distilled from metallic sodium. It was degassed in a vacuum at 2×10^{-6} hPa. It was then treated with 1,1-diphenylhexyllithium in hexane until the red color does not disappear. Toluene was condensed into the reaction vessel under high vacuum. Other solvents are distilled and—if necessary—were dried in the usual manner.

GPC: The PMMA polymers were investigated with a set-up consisting of a Hewlett-Packard 1084 B pump and a Waters differential refractometer 410. The Merck-Hitachi GPC integrator D-2520 was used for quantification. Columns from *Polymer Standard Service* SDV 10^3 and SDV 10^4 Å, each 5 μm, 30 cm/8 mm, were used in sequence. Elution medium: THF; 1.5 mL min^{-1}. Calibration by polystyrene standards.[25]

Preparation of the poly(trityl methacrylates) P I: The preparation of polymers **P I** was performed according to Okamoto's procedure.[18] In a vacuum line, tritylmethacrylate (12–20 g) was placed in a carefully degassed flask under argon (99.999%), and toluene (20 mL g^{-1} monomer) was condensed into it. After cooling to −78 °C, a definite amount of the initiator was added with a gas-tight syringe (molar ratio see Table 4). The initiator was prepared by placing a certain amount of N,N'-diphenylethylenediamine in a flask at a vacuum line and condensing toluene (around 5 mL) into it. At 0 °C, one equivalent of n-butyllithium (1.6 M in hexane) was added with a syringe. Under these conditions, the monolithium amide precipitated. It was dissolved by adding a 1.2-fold excess of (S,S)-1,4-bis(dimethylamino)-2,3-dimethoxy butane ((+)-DDB). In the case of **P I 9**, the corresponding (R,R)-compound ((−)-DDB) was used.

After 24 h at −78 °C, the polymerization was stopped by the addition of methanol (1 mL). The solution was evaporated to about half its volume, and the same amount of methanol was added. The precipitate was separated by centrifugation. The compound was reprecipitated from

Table 4. Preparation and properties of poly(trityl methacrylate) **P I** and poly(methyl methacrylate) **P III** in continuation of Table 1.[a]

Prepared polymer	Initiator/ monomer ratio	Yield	Prepared PMMA	M_w	M_n	M_w/M_n
P I 1	1:12	95	**P III 1**	3150	2 700	1.15
P I 2	1:15	98	**P III 2**	4550	3 950	1.15
P I 3	1:20	96	**P III 3**	5150	4 400	1.17
P I 4	1:20	96	**P III 4**	5100	4 500	1.13
P I 5	1:25	99	**P III 5**	6600	5 400	1.22
P I 6	1:25	97	**P III 6**	6950	5 850	1.18
P I 7	1:35	98	**P III 7**	8600	7 450	1.15
P I 8	1:50	95	**P III 8**	13050	10 900	1.19
P I 9	1:20	97	**P III 9**	4950	4 500	1.10

[a] Preparation of **P I** and **P III** according to the experimental part. Molar ratio of the initiator (monolithium amide of N,N'-diphenylethylenediamine) to the monomer (trityl methacrylate) is given. M_w and M_n are obtained from GPC measurements.[25] Polydispersities M_w/M_n are calculated from the original figures in Table 3; M_w and M_n values are rounded down.

benzene/*n*-hexane. The centrifugated compound was dried at 50 °C in vacuo. Yield: 90 – 98 %. The P_n of these polymers was obtained from GPC determination of the corresponding poly(methyl methacrylates) (Table 1 and Table 4).

Preparation of poly(diphenyl-2-pyridylmethyl methacrylates) P II: The preparation of **P II** was performed similarly as described for **P I**. The monomer was diphenyl-2-pyridylmethyl methacrylate[19] and as a catalyst, (+)-PMP was used. Details in Table 2 and Table 5.

Table 5. Preparation and properties of poly(diphenyl-2-pyridylmethyl methacrylate) **P II** and poly(methyl methacrylate) **P IV** in continuation of Table 2.[a]

Prepared polymer	Initiator/ monomer ratio	Yield	Prepared PMMA	M_w	M_n	M_w/M_n
P II 1	1:20	97	**P IV 1**	3400	3050	1.11
P II 2	1:28	97	**P IV 2**	4250	3900	1.09
P II 3	1:30	97	**P IV 3**	5250	4500	1.17
P II 4	1:30	95	**P IV 4**	5250	4600	1.13
P II 5	1:40	98	**P IV 5**	6700	6000	1.11
P II 6	1:50	98	**P IV 6**	9150	7850	1.16
P II 7	1:65	95	**P IV 7**	11100	9600	1.15
P II 8	1:80	95	**P IV 8**	13200	12050	1.09
P II 9	1:160	97	**P IV 9**	27100	24800	1.09
P II 10	1:160	98	**P IV 10**	30650	26050	1.17

[a] Preparation of **P II** and **P IV** as in Experimental Section. Molar ratio of the initiator (monolithium amide of *N,N'*-diphenylethylenediamine) to the monomer (diphenyl-2-pyridylmethyl methacrylate) is given. For M_w and M_n see Table 4.

Preparation of poly(methyl methacrylates) P III and P IV: Poly(trityl methacrylate) **P I** or poly(diphenyl-2-pyridylmethyl methacrylate) **P II** were suspended in methanolic HCl (5 %, 1 g in 150 mL) and were heated for 8 h (**P I**) and 24 h (**P II**), respectively, under reflux. The solution was evaporated to dryness, and the residue was dissolved three times in methanol and evaporated to remove the remaining HCl. The methanolic solution was then treated with diazomethane in diethyl ether until it stayed yellow, giving the methyl esters. After evaporation, the polymer was dissolved in methylene chloride and treated with methanol until the solution became turbid. Then, at 40 °C, the solvents were gradually removed until a polymer precipitated. Slow evaporation was continued in vacuo until most of the polymer was precipitated. The supernatant solution was then discarded, as it contained mostly oligomers. This procedure was repeated twice. The polymer was finally precipitated from dichloromethane/*n*-hexane. The purification procedure was followed by GPC. Yields: ≈ 60 %. Details in Tables 1, 2, 4, and 5.

Preparation of C_3-symmetric polymers P VI: The solution of the PMMA **P III** (1 equivalent) in dry dichloromethane (for example, 160 mg in 10 mL) was stirred at room temperature with triethylamine (1 equivalent) for 10 min. Then benzenetricarbonyl chloride (0.25 equivalents) in dichloromethane (10 % mL/mL) was added slowly. The reaction was monitored by GPC (Figure 1). After five days, the reaction was stopped, and the reaction mixture was worked up by precipitation in methanol. It was further purified by three precipitations from dichloromethane/methanol to remove low molecular weight compounds. The yields were between 20 – 30 %, based on the benzenetricarbonyl chloride.

P VI 4: ¹H NMR (CDCl₃): δ = 1.20 (s, 3 H; CH₃), 1.53, 2.15 (AB system, 2 H; CH₂), 3.60 (s, 3 H; OCH₃); ¹³C NMR (CDCl₃): δ = 21.96 (CH₃), 45.48 (C), 51.68 (OCH₃), 52.04 (CH₂), 176.49 (COO); elemental analysis [H-(C₅H₈O₂)₄₃-C₁₄H₁₄N₂]₃-C₉H₃O₃ (13708.0): calcd C 60.98, H 7.94, N 0.61; found C 60.81, H 8.07, N 0.68.

Preparation of a block copolymer P V of syndiotactic poly(methyl methacrylate) and poly(benzyl methacrylate): The initiator solution was prepared in freshly condensed toluene (50 mL) at – 78 °C. Triethylaluminium (0.75 mmol, 0.75 mL of a 1 M solution in hexane) and *tert*-butyllithium (0.25 mmol, 0.17 mL of a 1.5 M solution in pentane) were added to the toluene, followed by methyl methacrylate (4 mL, 38 mmol). After polymerizing for 24 h, an aliquot was taken out with a syringe. This part was used to characterize the PMMA block. Afterwards benzyl methacrylate (20 mmol,

3.5 g) was added to the toluene solution. The solution was allowed to warm to – 40 °C and was polymerized for another 24 h before the polymerization was stopped by the addition of methanol (1 mL). The polymer was precipitated by the addition of *n*-hexane (200 mL). The polymer was dried at 50 °C in vacuo.
MMA block: M_n = 14500, M_w = 17350, M_w/M_n = 1.20 (by GPC); percentage of syndiotactic triads (by NMR) = 87 %; block copolymer **P V**: M_n = 27900, M_w = 39200, M_w/M_n = 1.40 (by GPC); elemental analysis C₄H₉-[C₅H₈O₂]ₙ-[C₁₁H₁₂O₂]ₘ-H for *n* = 144 and *m* = 76 (27869.1): calcd C 67.26, H 7.45; found C 67.26, H 7.49.

Preparation of stereocomplexes of isotactic PMMA:[14, 20] Typically a solution of isotactic PMMA (21 mg) and of syndiotactic PMMA (125 – 150 mg, M_n ≈ 35000) or block copolymer **P V** in benzene (7 mL) was heated at 60 °C for 2 h. Afterwards, the samples were stored for 60 min at 20 °C and were cooled for 15 min with liquid N₂. The samples were stored at room temperature in the dark for two days. There was no visible precipitate or turbidity, but for better measurement of optical rotation, the solution was filtered through a membrane (regenerated cellulose, pore diameter 0.45 µm).

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