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Rational Approach to Stereochemical Analysis of Styrene–Methyl Methacrylate Copolymers through Synthesis of Appropriate Model Compounds

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ABSTRACT: Low molecular weight model compounds having closely analogous structures to certain stereochemical arrangements in copolymers of styrene and methyl methacrylate have been prepared. As a model for the central styrene unit in alternating styrene–methyl methacrylate copolymers the different 3,7-dimethyl-3,7-bis((methyloxy)carbonyl)-5-phenylnonanes were investigated. As models for central distyryl dyads the different 3,9-dimethyl-3,9-bis((methyloxy)carbonyl)-5,7-diphenylundecanes were prepared and investigated. With the help of ^{1}H, ^{13}C, and ^{1}H-^{13}C chemical shift correlation spectroscopy we have analyzed the comonomer sequence and stereochemical structures of these compounds and compared them with those of the copolymers reported earlier.

Introduction

Detailed understanding of the microstructure of synthetic vinyl polymers is of both fundamental and practical significance. The macroscopic physicomechanical and physicochemical properties of these materials are inherently dependent on their chain microstructures.[1-3]

The NMR technique has been proven to be the most powerful experimental tool for investigating the microstructures of vinyl homo- and copolymers.[4-6] This is due to the fact that the NMR chemical shifts are sensitive to the chemical and stereochemical structures of the different units constituting the chain to the closely bonded neighbors. Generally speaking, structural assignments of homopolymers are simpler than those of copolymers, since for the former the chemical shifts of different atoms are influenced by tacticity only. On the other hand, spectral patterns of copolymers are often complicated because the chemical shifts, in addition to being sensitive to the comonomeric compositional sequence distribution, are also influenced by the stereochemical arrangements of the monomer units (cotacticity) along the polymer chain. This gives rise to ambiguity for obtaining precise information on the microstructures of complex copolymer systems.

In the case of homopolymers the design of low molecular weight model compounds having structures closely analogous to those of polymers has been proven to be quite useful for analyzing the stereochemical features, as is evident from several recent publications.[7-10]

No such investigations have been reported with respect to copolymers. Hence, it appears interesting to design and synthesize low molecular weight model compounds possessing appropriate copolymer structures as aids in analysis of copolymer chain stereochemistry.

As a part of our ongoing research program on the design of stereoregular optically active vinyl homo- and copolymers,[11-14] we now report the results on the synthesis of styrene–methyl methacrylate (St–MMA) copolymer model compounds. Styrene–methyl methacrylate copolymers are one of the most thoroughly investigated copolymer systems for which ^{1}H and ^{13}C NMR techniques[15-17] and more recently 2D-NMR techniques[18] have been intensively utilized for elucidating their microstructural features.

With the help of ^{1}H, ^{13}C, and ^{1}H–^{13}C chemical shift correlation spectroscopy we have analyzed the comonomer sequence and stereochemical structures of these compounds and compared them with those of the copolymers reported earlier. The results of these studies are described in this paper.

Results and Discussion

Visualization of styrene–methyl methacrylate copolymer structures reveals that, depending on the relative placement of the substituents with respect to the plane of the polymer chain, seven possible triad arrangements consisting of styrene and methyl methacrylate units and having a styrene unit in the middle are in principle possible. They are depicted in Scheme I (M_mS_rM and M_rS_mM are identical).

The triad arrangements (M–S–M) are typical of those of alternating poly(styrene-*co*-methyl methacrylate) polymers. The chain stereochemistry of this copolymer has been investigated by Hirai et al.[17] We have synthesized model compounds for all possible triads of the S–S–M and M–S–M type and analyzed their configurational microstructures by NMR techniques.

Model Compounds of the M–S–M Type Triad Structure. The synthesis of the model compounds, i.e. with a styrene unit placed between two methyl methacrylate moieties, was accomplished by the procedure outlined in Scheme II.

Compound **3** is obtained by a coupling reaction between dibromide **1b** and the ester enolate of methyl 2-methylbutyrate **2**. Compound **1b** was synthesized by the treatment of 2-phenyl-1,3-propanediol (obtained by $LiAlH_4$ reduction of phenylmalonic acid diethyl ester[19]) with tetrabromomethane/triphenylphosphine reagent.[20] The product **3** was isolated in purified form by preparatice GPC. Spectral and elementary analysis data confirm the purity of the isolated compound.

The distribution patterns of the stereoisomers of **3** formed during the coupling reaction can be investigated by ^{1}H and ^{13}C NMR spectroscopy.

In the ^{1}H NMR spectra of alternating copolymers the α-methyl and methoxycarbonyl protons are reported to be particularly sensitive to the different mode of arrangements of the neighboring monomer units.[17,18] The ^{1}H NMR spectrum of **3** shows multiple resonance lines for

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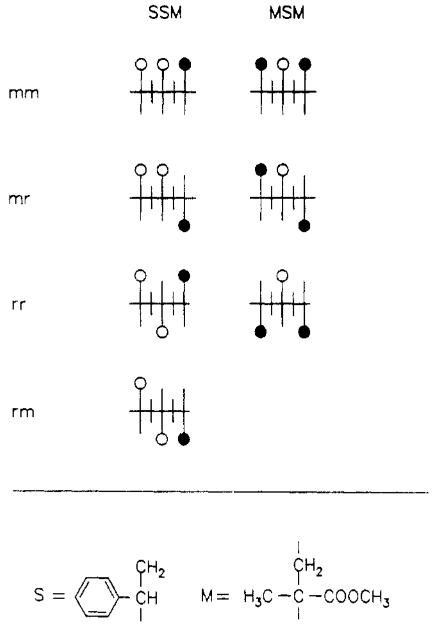
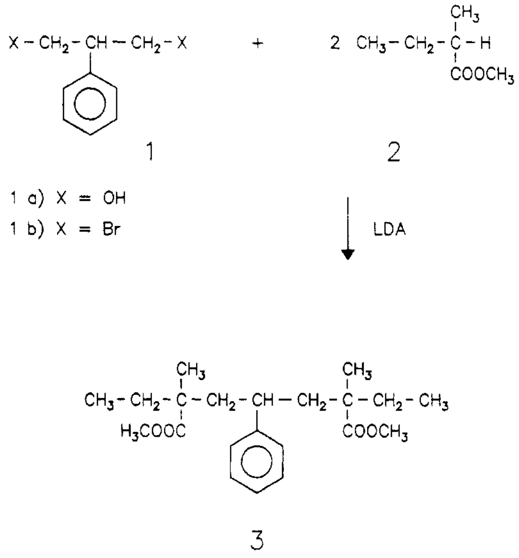
Scheme I
Possible Copolymeric Triads with Styrene–Methyl Methacrylate Units Having Styrene as the Central Unit



Scheme II
Synthesis of Model Compounds Having a Styrene Unit Placed between Two Methyl Methacrylate Moieties



LDA = Lithiumdiisopropylamid

both these groups, thus suggesting a random distribution of stereoisomers.

The conceivable stereoisomers for **3** are depicted in Scheme III. With reference to the alternating copolymer of MMA and styrene, **3a**, **3b**, and **3d** correspond to the coiso-, cohetero-, and cosyndiotactic triad structures. The coheterotactic arrangements M_mS_rM and M_rS_mM (**3b** and **3c**) are not distinguishable.

The methoxycarbonyl protons (ca. 3.03–3.47 ppm) and the α-methyl protons (ca. 0.89–1.10 ppm) each give rise to four resonance lines. They were assigned on the basis of consideration of shielding effects of the phenyl ring current.[18] Besides this type of signal assignment based on shielding due to aromatic ring current effect, we have independently established our assignments with the help of NOE-difference experiments, which are possible for these model compounds but not for polymers. Irradiation of the upfield methoxy protons (3.03 ppm) results in a relative NOE of 6.8% for the aromatic protons, while irradiation of the methoxy protons at 3.47 ppm (cosyndio triad system) brings about only 3.2% of relative NOE for the aromatic protons. This clearly attests to our assignments of the different resonance lines to the individual diastereomers.

Scheme III
Conceivable Stereoisomers of 3 (3b and 3c Not Distinguishable)

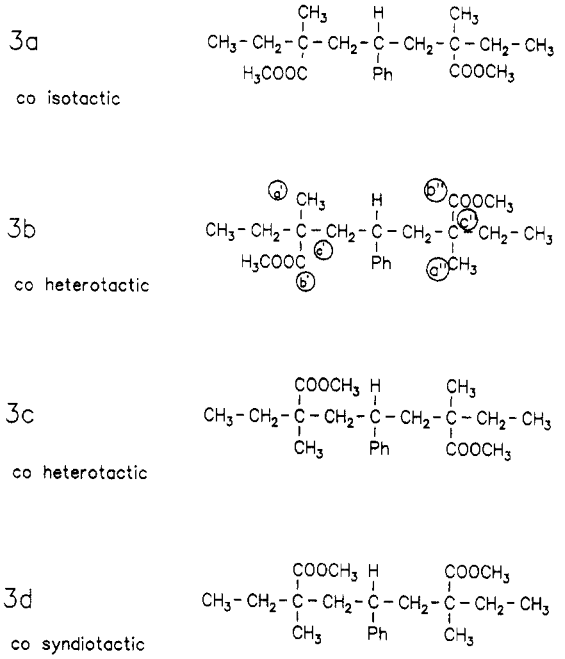


Table I
Assignments of Diastereomers in Compound 3 from the ^{1}H NMR Chemical Shifts of MethoxyCarbonyl and α-Methyl Proton Resonances

structure type	triad arrangement	chemical shift (ppm)	
		α-methyl ^{1}H resonance	methoxy ^{1}H resonance
3a	M_mS_mM	1.093	3.03
3b, 3c	M_mS_rM	1.086 (a′)	3.08 (b′)
		0.93 (a″)	3.42 (b″)
3d	M_rS_rM	0.89	3.47

The upfield signal at 3.03 ppm for the methoxy proton resonances is assigned to **3a**, and the one at 3.47 ppm, to **3d**. This assignment is in accordance with that of Hirai et al.[17] put forward for alternating copolymers of styrene and methyl methacrylate. The ester groups in these two compounds are magnetically equivalent (mirror plane) and thus give only one signal. Structure **3b** represents the model for a coheterotactic triad. A close examination of this structure reveals that each of the two ester groups has a different environment (comeso and coracemic diad) and therefore appears at different chemical shifts (b′ at 3.08 ppm for the comeso diad, and b″ at 3.42 ppm for the coracemic diad).

For the α-methyl resonances similar effects, though less pronounced, are expected for the different diastereomers[18a] but in the reverse order of chemical shift. Thus on the basis of shielding effect considerations and NOE-difference experiments the signal assignments were carried out and the results are summarized in Table I.

In addition to the ^{1}H NMR experiments, ^{13}C NMR investigations of compound 3 were carried out to further confirm the assignment of different diastereomeric structures. Apart from being free from the spin–spin coupling problems, ^{13}C NMR provides the additional advantage of

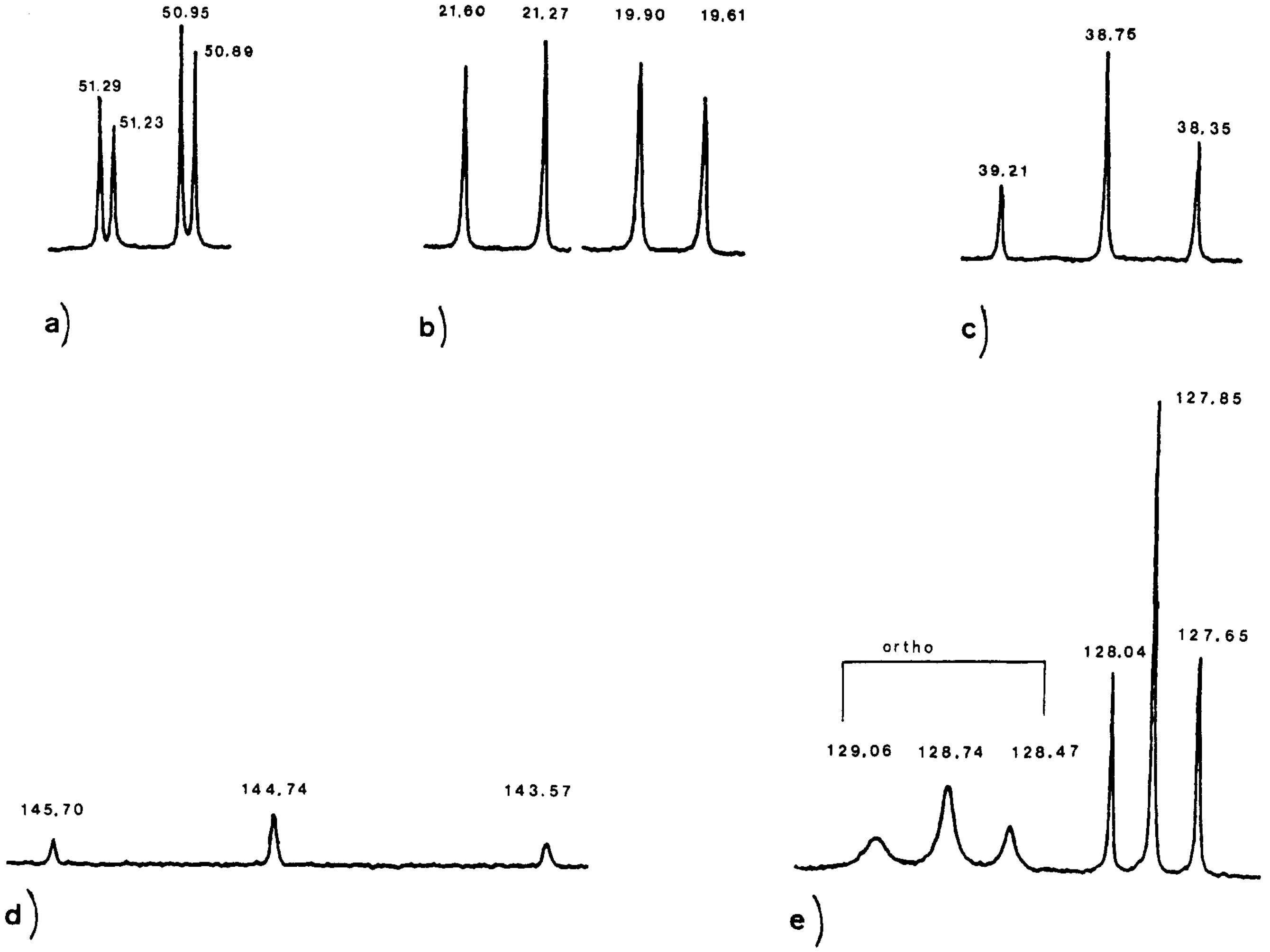


Figure 1. Expanded ^{13}C NMR spectral pattern at 75.4 MHz of the representative carbon atoms of **3**: (a) methoxy; (b) α-methyl; (c) backbone methine; (d) aromatic ipso; (e) aromatic ortho and aromatic meta carbon atoms.

a wider range of chemical shift dispersion and hence greater sensitivity to structural details.

At first we consider the ^{13}C NMR signals of the methoxy carbons and the α-methyl carbon atoms for which the proton NMR signal assignments for different diastereomers have been established (see Table I). As can be seen from the expanded spectral pattern (Figure 1a), the methoxy carbon atoms, which resonate in the region 50.89–51.29 ppm, show four resonance lines like its proton counterpart. The signals have been assigned as cosyndio-, cohetero- (both the middle peaks), and coisotactic triad types with increasing order of magnetic field. Similarly, the α-methyl carbon atoms show four resonance lines in the region 19.61–21.60 ppm (Figure 1b) corresponding to the three different diastereomers. In order to provide an additional experimental basis for unambiguous signal assignment, we have employed two-dimensional correlation spectroscopy (COSY NMR technique). In recent years this technique has been quite successfully utilized for the analysis of stereochemical features of synthetic polymers.[21,22]

Examination of the spectrum reveals that for the methoxy groups the upfield proton signals correlate with the upfield carbon signals and the downfield signals with the corresponding downfield ones, thus confirming our signal assignments. For the α-methyl group, the shift correlation shows an unexpected feature, namely the upfield proton peaks map with the downfield carbon signals and vice versa. This situation is different from the assignments reported for the copolymer systems[21,22] and merits further investigations on the assignments in the copolymers.

Table II
Assignments of Diastereomers in Compound 3 from the ^{13}C NMR Chemical Shifts of the ^{13}C Signals of the MMA Moiety

		chemical shift in various carbon resonances (ppm)			
structure type	triad arrangements	α-methyl carbon	methoxy carbon	carbonyl carbon	backbone quaternary carbon
3a	M_mS_mM	19.61	50.89	176.64	47.56
3b, 3c	M_mS_rM	19.90 (a′) 21.27 (a″)	50.95 (b′) 51.23 (b″)	176.72 (b′) 177.38 (b″)	47.60 (c′) 48.17 (c″)
3d	M_rS_rM	21.60	51.29	177.50	48.33

Apart from these two signals, other carbons of the MMA unit, i.e., the carbonyl and the quaternary carbon atoms, are also sensitive to diastereomeric effects. Assignments of these signals to the different diastereomers were made in light of the alternating styrene–MMA copolymer assignments.[17] These results are summarized in Table II.

More relevant in the stereochemical investigation of these copolymer analog model compounds is the structural analysis with respect to the phenyl ring in **3**, since it represents the central unit of the MSM triad whereas the methyl methacrylate units have only neighbors at one side. The ^{1}H NMR analysis is prohibitive due to spin–spin coupling and therefore analysis of ^{13}C signals was only pursued for this part. In this case the aromatic C-1 carbon atom (ipso carbon atom) and the backbone methine carbon atom of the styrene moiety have already been intensively investigated in the case of alternating copolymers.[17]

It is evident from Figure 1c,d that for compound **3** each of these carbons shows three signals corresponding to the

Table III
Assignments of Diastereomers in Compound 3 from the ^{13}C NMR Chemical Shifts of the ^{13}C Signals of the Aromatic Moiety

		chemical shift (ppm)			
structure type	triad arrangements	backbone methine carbon	ipso carbon	ortho carbon	meta carbon
3a	M_mS_mM	38.35	143.57	128.47	127.65
3b, **3c**	M_mS_rM	38.75	144.74	128.74	127.85
3d	M_rS_rM	39.21	145.70	129.06	128.04

different diastereomers. The three resonance lines for the C-1 carbon appear at 143.57, 144.74, and 145.70 ppm, and those of the methine carbon atom, at 38.35, 38.75, and 39.21 ppm. In the case of the copolymer, the three resonance lines of aromatic C-1 appeared at 142.8, 144.7, and 146.6 ppm and those of backbone methine, at 37.3, 38.4, and 38.9 ppm.[17,18a] Our assignments of the signals for **3** given in Table III are in accordance with those in the copolymers. It was possible for the first time also to designate the signals of the aromatic ortho and meta carbon atoms. The results of their assignments are also summarized in Table III.

The extent of formation of different diastereomers during the coupling reaction can be estimated from the relative peak intensities. The relative intensities of the signal lines indicate a 1:2:1 ratio for the phenyl unit and 1:1:1:1 for the MMA unit. This suggests that during the formation of **3**, i.e. the alkylation of an ester enolate, which is not stereochemically controlled, the relative amounts of the different diastereomeric triad analogs thus produced follow a Bernoullian type distribution pattern.

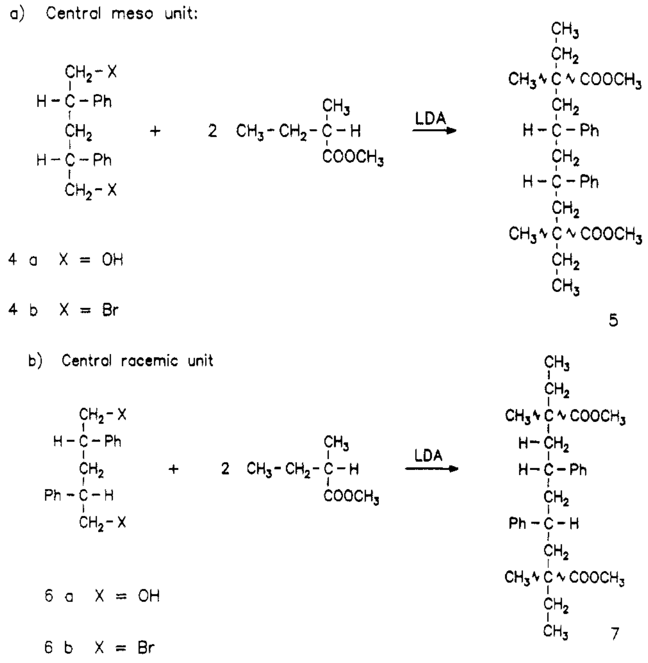
Synthesis of Model Compounds Having S–S–M Type Triad Structures. The second type of comonomer sequence triad realized in copolymer structures is of S–S–M type. For this type (monomer sequence) several possible stereochemical arrangements (cotacticities) are also anticipated. The appropriate models analogous to this chain structure would be well-defined distyryl diads flanked by two MMA units, i.e. a MSSM type structure. In order to minimize the formation of a large number of diastereomers, we started with pure meso and racemic forms of the distyryl diads, which were subsequently alkylated with the appropriate ester enolates. The synthetic approaches for obtaining these M–S–S–M compounds are outlined in Scheme IV.

Synthesis of *meso*- and *rac*-1,5-dihydroxy-2,4-diphenylpentanes (**4a** and **6a**) and their conversion to the corresponding dibromides have been described earlier.[12]. These dibromides (**4b** and **6b**) were reacted with the ester enolate of methyl 2-methylbutyrate (**2**), yielding **5** and **7**. The desired products were purified by preparative GPC, and their purity was established from satisfactory mass spectral and elemental analysis data. The stereochemical features of these compounds were elucidated by means of NMR spectroscopy.

By using distyryl diads of predetermined stereochemistry (meso or racemic) the number of possible diastereomers amounts to three in each case. Since the alkylation reaction is stereochemically nonselective, the newly generated stereogenic centers in the MMA units are randomly distributed. For a particular distyryl diad the expected possible diastereomers are illustrated in Scheme V.

Examination of the two sets of structures, i.e. **5a–d** and **7a–d**, indicates that structures **5b** and **5c** as well as **7b** and **7c** are identical, and hence three types of diastereomers result for each of these two M–S–S–M tetrad types.

Scheme IV
Synthetic Routes toward MSM Type Compounds



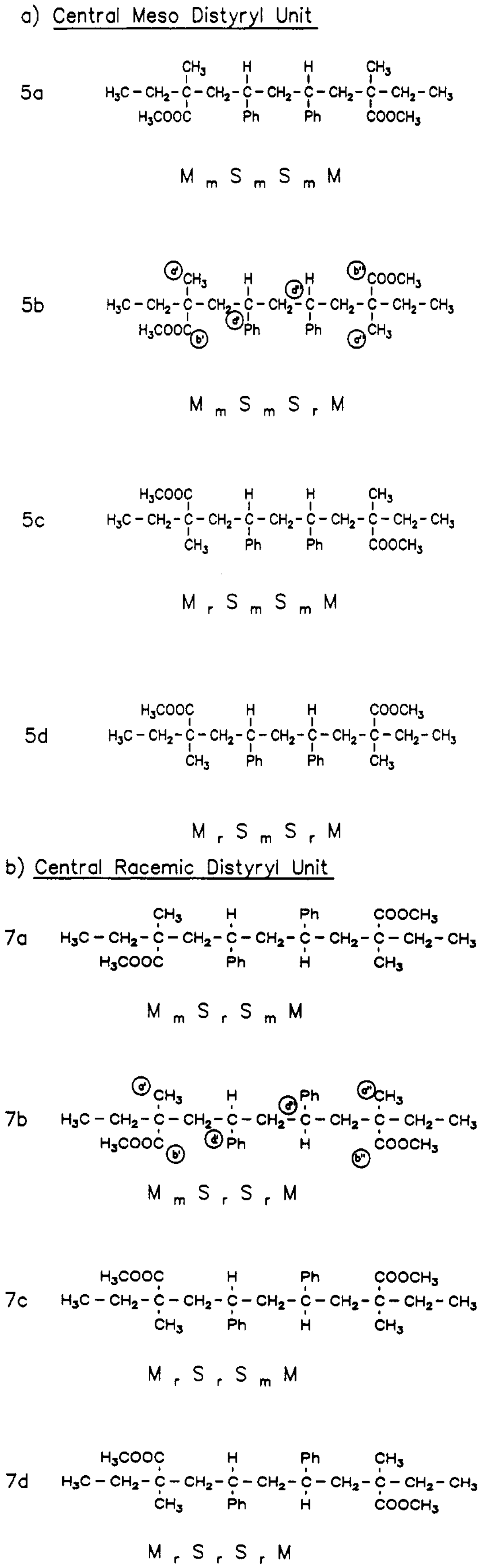
At first the ^{1}H NMR spectra of these compounds were analyzed. Similar to the case of **3**, only the α-methyl and the methoxycarbonyl protons provide precise configurational information. The information from other protons is dampened by spin–spin coupling. The expanded spectral patterns of these two types of protons of **5** and **7** are depicted in Figure 2. For the meso and racemic compounds these two groups of protons reveal each four resonance lines. The chemical shifts of the individual signals are different for **5** and **7**, as is illustrated for their mixture in Figure 2, suggesting the influence of the relative configurations of distyryl diads on the chemical shift of the different diastereomers.

For the α-methyl protons, all the four resonance lines of the MS_rSM compound **7** appear at higher field compared to its meso counterpart **5**. For the methoxycarbonyl protons, the signals of **7** lie between those of **5**. The chemical shift differences for the individual diastereomers are higher for the system having a central meso unit, i.e. **5**.

On the basis of aromatic ring current shielding considerations, the upfield signals of the methoxycarbonyl protons were assigned as M_mS_mS and M_mS_rS triad arrangements and the downfield signals, as M_rS_mS and M_rS_rS triad arrangement. Furthermore, the appearance of four resonance lines can be explained on the basis of the dissimilarities in electronic shielding of the protons placed on the same or opposite site of the phenyl rings (**5b** and **7b**). Interestingly, there are still differences, though relatively small, between chemical shifts of the α-CH_3 and methoxycarbonyl protons in **5a** and **7a**, compared with those of the a′ and b′ in **5b** and **7b**, respectively. This implies that the influence of configurational differences in the third monomeric unit is still noticeable. The same holds well while the resonances of the a″ and b″ groups of **5b** and **7b** are compared with those of **5d** and **7d**, respectively. The details of the assignments of the signals and the chemical shifts of the different diastereomers are summarized in Table IV.

The proton-noise decoupled ^{13}C NMR spectra of **5** and **7**, too reveal sensitivity to diastereomeric effects, as discussed earlier for the M–S–M type. At first, we again discuss the α-methyl and methoxycarbonyl resonances.

Scheme V
Possible Diastereoisomers in MSSM Type Oligomers



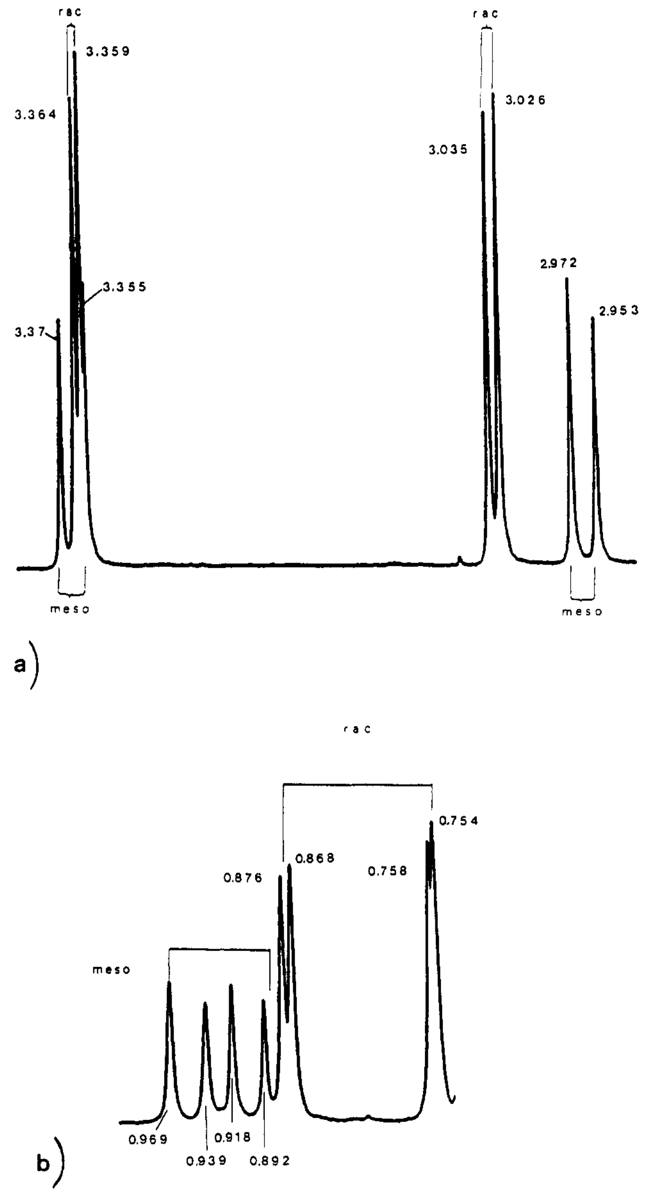


Figure 2. Expanded spectral pattern of the ^1H resonances at 300 MHz of representative groups in **5** and **7** in a 1:1.7 molar mixture: (a) methoxy protons; (b) α-methyl protons.

Table IV
Assignments of Diastereomers in Compounds 5 and 7 from the ^1H NMR Chemical Shifts of the ^1H Signals of the MMA Moiety (See Also Scheme V)

structure type	tetrad arrangements	chemical shift (ppm) α-methyl proton	chemical shift (ppm) methoxy carbonyl proton
5a	$M_mS_mS_mM$	0.97	2.96
5b, 5c	$M_mS_mS_rM$	0.94 (a′) 0.92 (a″)	2.98 (b′) 3.36 (b″)
5d	$M_rS_mS_rM$	0.89	3.38
7a	$M_mS_rS_mM$	0.88	3.02
7b, 7c	$M_mS_rS_rM$	0.87 (a′) 0.76 (a″)	3.04 (b′) 3.36 (b″)
7d	$M_rS_rS_rM$	0.75	3.37

As can be seen from the expanded spectral pattern in Figure 3, these two carbon atom types for both **5** and **7** show four resonance lines. The chemical shifts are different for **5** and **7**. This attests to the influence of the configuration of the central distyryl diad on the chemical shifts of the different isomers. The ^{13}C assignments for **5** and **7**, derived similarly as in the case of **3** and coupled with 2D-HECTOR experiments, are summarized in Table V.

As the aromatic part of these compounds represents the central unit of these copolymer analog model structures, analysis of their ^{13}C resonances is especially interesting. In particular, we intend to discuss the resonances

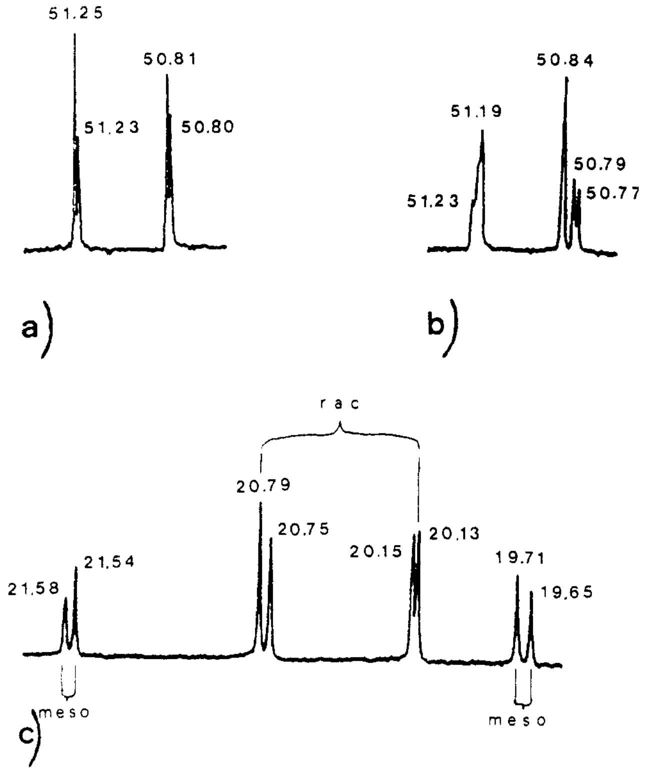


Figure 3. Expanded spectral pattern of the carbon-13 resonances of the MMA part of **5** and **7**: (a) methoxy carbon resonances of **5**; (b) methoxy carbon resonances and (c) α-methoxy carbon resonances of a 1:1.7 molar mixture of **5** and **7**.

Table V
Assignments of Diastereomers in the Compounds 5 and 7 from the ^{13}C NMR Chemical Shifts of the ^{13}C Signals of the MMA Moiety

		chemical shift in various carbon resonances (ppm)		
structure type	tetrad arrangements	α-methyl carbon	methoxy carbon	carbonyl carbon
5a	$M_mS_mS_mM$	19.66	50.80	176.75
5b, **5c**	$M_mS_mS_rM$	19.72 (a′) 21.55 (a″)	50.81 (b′) 51.23 (b″)	176.78 (b′) 177.47 (b″)
5d	$M_rS_mS_rM$	21.59	51.25	177.51
7a	$M_mS_rS_mM$	20.13	50.77	176.85
7b, **7c**	$M_mS_rS_rM$	20.15 (a′) 20.75 (a″)	50.79 (b′) 50.19 (b″)	176.88 (b′) 177.61 (b″)
7d	$M_rS_rS_rM$	20.79	51.21	177.61

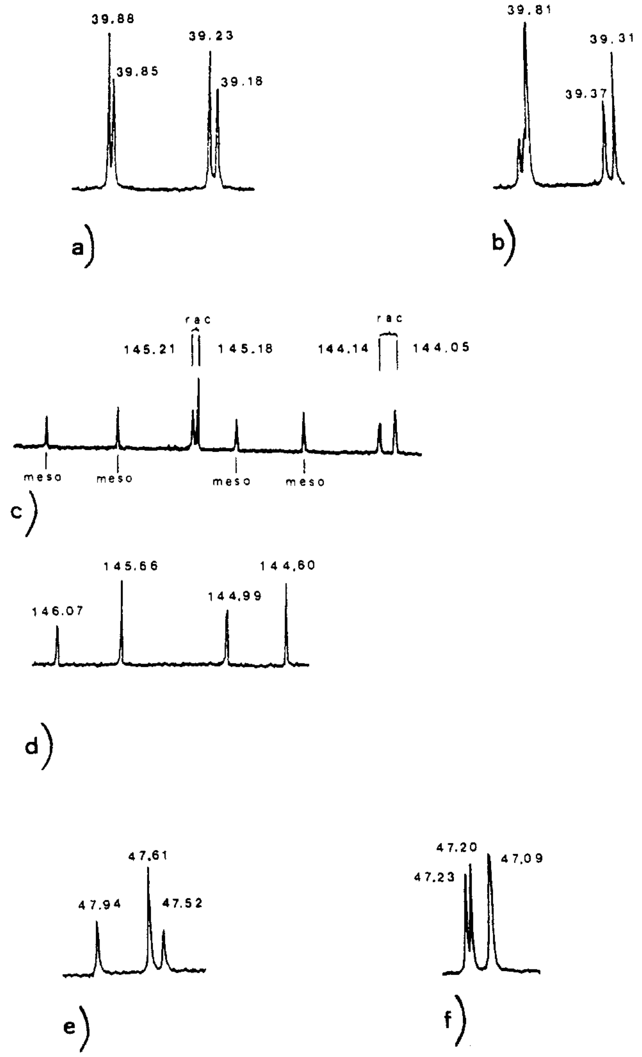


Figure 4. Expanded spectral pattern of the carbon-13 resonances of the distyryl part of **5** and **7**: (a) backbone methine of **5**; (b) backbone methine of **7**; (c) ipso carbon of a 1:1.7 molar mixture of **5** and **7**; (d) ipso carbon of **5**; (e) central methylene carbon of **5**; (f) central methylene carbon of **7**.

Table VI
Assignments of Diastereomers in the Compounds 5 and 7 from the ^{13}C NMR Chemical Shifts of the ^{13}C Signals of the Aromatic Moiety

		chemical shift in various carbon resonances (ppm)		
structure type	tetrad arrangements	backbone methine	aromatic ipso carbon	$-CH_2-$ carbon between two phenyl rings
5a	$M_mS_mS_mM$	39.18	144.60	47.52
5b, **5c**	$M_mS_mS_rM$	39.23 (d′) 39.85 (d″)	144.99 (d′) 145.66 (d″)	47.61
5d	$M_rS_mS_rM$	39.88	146.07	47.94
7a	$M_mS_rS_mM$	39.31	144.05	47.09
7b, **7c**	$M_mS_rS_rM$	39.37 (d′) 39.81 (d″)	.144.14 (d′) 145.18 (d″)	47.20
7d	$M_rS_rS_rM$	39.81	145.21	47.23

of the C-1 carbon of the phenyl ring (ipso carbon atom), the backbone methine carbon atom carrying the phenyl ring, and the backbone methylene carbon atom flanked by two aromatic rings (see Figure 4). For styrene–MMA copolymers the ipso carbon atom has already been analyzed but only for sequence analysis.[16] In the starting materials, the *meso*- and *rac*-1,5-dibromo-2,4-diphenylpentanes **4b** and **6b**, these three carbon atoms show single resonance lines. For **4b** they appear respectively at 141.76, 44.91, and 38.27 ppm, and for **6b** they appear respectively at 140.81, 45.44, and 37.37 ppm. In the diastereomers of the model compounds **5** and **7** they reveal four resonance lines of nearly equal intensity for the aromatic ipso carbon atoms as well as for the backbone methine carbon atoms. Three resonance lines of 1:2:1 intensity ratio are obtained for the central methylene carbon atom. Different numbers of signals observed for these carbon atoms can be justified from the consideration of the symmetry position of these groups in the molecule. Whereas the methylene groups for each diastereomer can only give one signal in **5b** and **7b**, respectively, the two ipso carbon atoms and the two methine carbon atoms for these structures are not magnetically equivalent (d′ and d″). Assignments of these signals to different diastereomers and their chemical shifts are summarized in Table VI. A comparison of the chemical shifts of these resonance lines for **5** and **7** suggests that the differences in the chemical shifts of these diastereomers is larger for the isomer containing the meso distyryl diads compared to that with the racemic diads.

Conclusion

Two types of low molecular weight model compounds having structures analogous to styrene–methyl methacrylate copolymers were synthesized, where styrene constitutes the central unit and is flanked by MMA units (M–S–M, M–S–S–M). The analysis of their NMR spectra enabled the assignments of the ^1H and ^{13}C resonance signals to their different stereochemical structures. For this purpose, in addition to aromatic ring current shielding considerations, NOE experiments and 2D experiments (COSY) (heteronuclear) were performed. These studies would facilitate the interpretation of copolymer NMR spectra with greater confidence. In this respect the spectral features of the MMA units were only used for structure elucidation of the model compounds since the MMA has only on one side a comonomeric unit. On the other hand in this case stereochemical differences in the first, the second, and the third comonomeric unit can be identified in the NMR spectra of the MMA unit.

More importantly, for the first time sequence and diastereomeric differences in the styrene moiety could be identified unambiguously. Even if on both sides of the styrene moiety only one or two comonomeric units were attached, valuable informations was obtained. If more comonomeric units were attached on both sides of the styrene moiety, a large number of diastereomeric structures would be generated which would complicate the signal assignments. Therefore we started with one or two units on both sides. For the different diastereomeric structures the ^{13}C NMR spectral analysis of the ipso carbon atom of the phenyl ring is best suited. Further possibilities are in the methine and methylene groups of the styrene moiety as well as in the ortho and meta carbon atoms of the phenyl ring.

Experimental Section

Materials and Methods. The reagents were purchased either from Fluka AG or E. Merck as reagent grade or analytical grade chemicals. The analytical grade reagents were used as received, and the reagent grade chemicals were purified either by distillation or recrystallization prior to use. The solvents used were of reagent grade and were purified by standard procedures immediately prior to use.

Elemental analyses were performed in the microanalytical laboratory of the Faculty of Natural Sciences, University of Düsseldorf. ^1H and ^{13}C NMR spectra were recorded with a Varian VXR-300 spectrometer operating at 300 and 75.4 MHz for ^1H and ^{13}C nuclei, respectively. The spectra were obtained in $CDCl_3$ solution with TMS as the internal reference. Mass spectra were obtained with a Varian MAT CH 50 spectrometer. GPC separations were carried out using a DuPont chromatographic pump with a preparative GPC column (Ostion LGC 6% Chemapol Praha) and with THF as the eluent.

Synthesis of 1,3-Dibromo-2-phenylpropane (1b). To a solution of 3 g (19.7 mmol) of 1,3-dihydroxy-2-phenylpropane (**1a**, obtained by $LiAlH_4$ reduction of phenylmalonic acid diethyl ester[19]) and 16.6 g (50 mmol) of tetrabromoethane in 50 mL of methylene chloride cooled to 0 °C was added dropwise under nitrogen atmosphere 13.2 g (50 mmol) of triphenylphosphine dissolved in 80 mL of methylene chloride. After completion of addition, the reaction mixture was slowly allowed to warm to room temperature and stirred for an additional 3 h. Methanol was added to decompose the excess $CBr_4/P(C_6H_5)_3$ complex, and the solvent was removed under reduced pressure. The resulting residue was treated with diethyl ether/methylene chloride (80:20 v/v) and filtered off, and the solvent was evaporated. Finally, the residue was dissolved in diethyl ether and the solution was filtered through a pad of Al_2O_3 (neutral) to separate out triphenylphosphine oxide. The filtrate was concentrated and purified by vacuum distillation (Kugelrohr, 140 °C, 10^{-1} Pa), yielding 3.4 g (62%) of **1b**. ^1H NMR: δ 3.52 (d, 4 H, $-CH_2Br$), 2.8 (m, 1 H, phenyl *CH*), 7.15 (m, 5 H, phenyl). Mass spectrum: *m/e* 278 (M^+). Anal. Calcd for $C_9H_{10}Br_2$: C, 38.88; H, 3.62. Found: C, 38.43; H, 3.68.

Synthesis of *meso*- and *rac*-1,5-Dibromo-2,4-diphenylpentanes (4b and 6b). These two compounds were prepared from the respective dihydroxy precursors (**4a** and **6a**) in a manner similar to the above described procedure. The detailed methods of the synthesis of these dihydroxy and dibromo compounds have been reported in our earlier publication.[12]

Coupling Reactions. All these reactions were carried out in flame-dried apparatus under argon atmosphere.

Reaction of 1,3-Dibromo-2-phenylpropane with Methyl 2-Methylbutyrate. A sample of 2.4 g (20.5 mmol) of methyl 2-methylbutyrate (**2**) was converted to the ester enolate according to the method of Lochmann et al.[23] (LDA, THF, −78 °C). To this ester enolate was added at −70 °C a solution of 1.5 g (5.4 mmol) of **1b** in 10 mL of DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone)[23] and the solution was stirred at this temperature for 1 h. The reaction mixture was slowly warmed to −40 °C and stirred at this temperature for 2 days. At the end of the reaction, methanol was added to decompose unreacted enolate anions. The reaction mixture was treated with 100 mL of water, was stirred for 1 h, and extracted with diethyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The pure product **3** was isolated by preparative GPC using THF as eluent (40% yield). Mass spectrum: *m/e* 336 (M^+). Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.58. Found: C, 71.05; H, 9.64. ^1H and ^{13}C NMR gave satisfactory data, and the results are discussed in the Results and Discussion.

Reaction of *meso*-1,5-Dibromo-2,4-diphenylpentane (4b) with Methyl 2-Methylbutyrate (2). By treatment of the ester enolate of **2** (1.8 g, 16 mmol) with 1.5 g (4 mmol) of **4b** in a manner analogous to the synthesis of **3** and after usual workup and GPC purification, the product **5** (52% yield) was obtained. Mass spectrum: *m/e* 452 (M^+). Anal. Calcd for $C_{29}H_{40}O_4$: C, 75.95; H, 8.91. Found: C, 75.62; H, 9.04.

Reaction of *rac*-1,5-Dibromo-2,4-diphenylpentane (6b) with Methyl 2-Methylbutyrate (2). Employing the analogous procedure for the synthesis of **5**, this coupling reaction yielded **7**. Mass spectrum: *m/e* 452 (M^+). Anal. Calcd for $C_{29}H_{40}O_4$: C, 75.95; H, 8.91. Found: C, 75.53; H, 9.07.

The NMR spectra of these compounds gave satisfactory information and have been dealt with in detail in text.

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Supplementary Material Available: Figures of original NMR spectra for **3** and **5** (10 pages). Ordering information is given on any current masthead page.

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Registry No. **1a**, 1570-95-2; **1b**, 85291-68-5; **2**, 868-57-5; **3a**, 143216-85-7; (±)-**3b**, 143290-37-3; **3d**, 143290-38-4; **4b**, 110590-57-3; **5a**, 143216-87-9; (±)-**5b**, 143290-39-5; (±)-**5d**, 143290-40-8; (±)-**6b**, 143216-86-8; (±)-**7a**, 143290-41-9; (±)-**7b**, 143290-42-0; (±)-**7d**, 143291-51-4; $Br_2(CH)_2Br_2$, 558-13-4; styrene–methyl methacrylate (copolymer), 25034-86-0.