

Microstructural Analysis of Methyl Methacrylate–Lauryl Methacrylate Copolymers Using ^{13}C NMR Spectroscopy

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ABSTRACT: ^{13}C NMR spectra (75.5 MHz) of methyl methacrylate (M)–lauryl methacrylate (L) copolymers prepared by group transfer polymerization (GTP) were analyzed for sequence distribution and relative stereochemical configuration of monomer units along the macromolecular chains. The concentrations of M- and L-centered triads, determined experimentally from $\alpha\text{-CH}_3$ and $\text{C}=\text{O}$ resonance signals, were in good agreement with those calculated statistically, taking into consideration the terminal copolymerization model and Bernoullian distribution of stereoregularity, with the statistical parameters P_{ij} determined from the reactivity ratios $r_{\text{M}}=1.38\pm 0.11$ and $r_{\text{L}}=0.68\pm 0.10$ and the coisotacticity parameters $\sigma_{\text{MM}}=0.24$, $\sigma_{\text{LL}}=0.27$, $\sigma_{\text{ML}}=\sigma_{\text{LM}}=\sigma^*=0.30$.

KEY WORDS Group Transfer Polymerization / ^{13}C Nuclear Magnetic Resonance / Polymer Microstructure / Methyl Methacrylate / Lauryl Methacrylate / (1-Methoxy-2-methyl-1-propenyl)oxy-trimethylsilane / Tetrabutylammonium Bibenzoate / Tetrahydrofuran /

Group Transfer Polymerization (GTP) makes possible the synthesis of random and block copolymers with good control of molecular weight and distribution. Copolymers of methyl methacrylate (MMA) with higher alkyl methacrylates, such as lauryl methacrylate (LMA) exhibit interesting properties on account of their comblike structures. Controlled synthesis of such polymers is not possible by anionic techniques since living anionic polymerization of alkyl methacrylates is feasible only below -50°C in tetrahydrofuran (THF), under which condition LMA has no solubility in the solvent. Thus, GTP is the only available synthetic method for preparing narrow molecular weight distribution random and block copolymers of MMA and LMA. We recently reported the preparation of random copolymers of MMA and LMA spanning a wide composition range.¹

^{13}C NMR spectroscopy is useful for the analysis of chemical structure, morphology, orientation and molecular dynamics of a polymer chain² all of which have an effect on material properties. The properties of a copolymer depend both on the chemical nature of the repeating units and on their arrangement within the polymer chain.

Detailed microstructural analysis of acrylic ester copolymers synthesized by GTP has not been reported in the literature. This paper examines the detailed microstructure of these copolymers using ^{13}C NMR spectroscopy.

EXPERIMENTAL

Copolymerization

The copolymers of MMA and LMA with varying feed compositions were prepared by using (1-methoxy-2-methyl-1-propenyl)oxytrimethylsilane (MTS) and tetrabutylammonium bibenzoate (TBABB) as a initiator and catalyst in THF at room temperature.¹ Precipitation in methanol and evaporation of solvent gave the random

copolymers. The conversions of these copolymers were restricted to a low range as described in Table I.

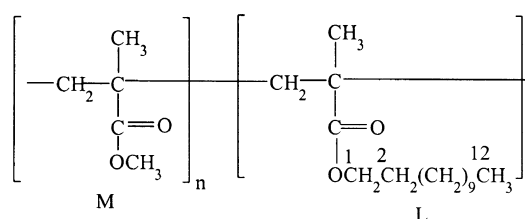
^{13}C NMR Spectra Measurements

^{13}C NMR spectra were recorded at 75.5 MHz (Bruker MSL-300) spectrometer at 393 K. The sample concentration was 15% w/v in 1,2,4-trichlorobenzene. C_6D_6 (10%) was used as the external reference in a sealed capillary tube as locking agent. Spectra were obtained by using BROADBAND decoupling and a pulse delay of 2 s, accumulating 12000 scans with digital resolution of 0.4 Hz point⁻¹, corresponding to a spectral width 25000 Hz and a data length of 16 K. The flip angle and acquisition time were 60° and 1.3 s, respectively. These conditions ensure the complete relaxation of all the nuclei analyzed. Relative peak intensities were measured from peak areas calculated by means of electronic integration or by triangulation and planimetry.

RESULTS AND DISCUSSION

GTP of MMA with LMA in THF solution, using TBABB as catalyst and MTS as initiator at room temperature, gives rise to the formation of homogeneous random copolymers with statistical distribution of monomer units along the polymer chain which corresponds to the chemical structure outlined in Scheme 1.

The average molar compositions of different copolymer samples prepared at conversions $<15\%$ were determined from analysis of the corresponding ^1H NMR



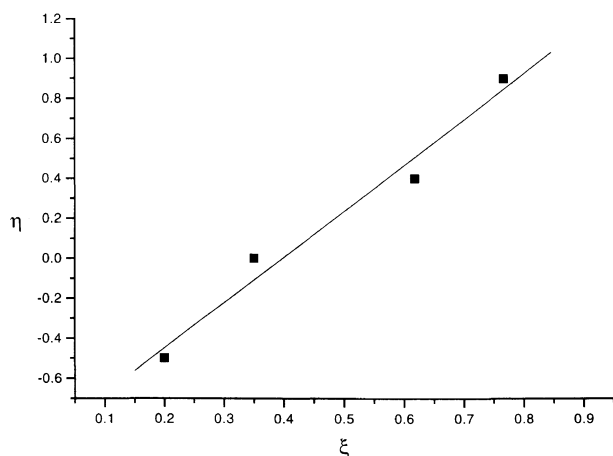
Scheme 1.

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Table I. Compositions and conditional probabilities P_{ij} for the copolymerization at low conversion of methyl methacrylate (M) with lauryl methacrylate (L)

Feed F_M^a	f_M^a (copolymer)		P_{ML}	P_{LM}
	^1H NMR	^{13}C NMR		
0.190	0.267	0.243	0.755	0.256
0.390	0.501	0.491	0.531	0.484
0.608	0.641	0.654	0.318	0.695
0.795	0.838	0.848	0.157	0.850

^a F_M and f_M are molar fractions of methyl methacrylate in the monomer feed and in the copolymer samples, respectively.


Figure 1. Determination of the monomer reactivity for the GTP of MMA and LMA according to the Kelen and Tüdös method, $\alpha=0.75$.

spectra (Table I). The compositions of the copolymers were also determined from the ^{13}C spectra.

Copolymer composition was determined from analysis of the signal assigned to the $-\text{OCH}_3$ group (δ 51.39) of M units and $-\text{OCH}_2$ group (δ 64.21) of L units. These signals appear as very sharp peaks in the spectra of the copolymers⁵ and their relative intensities are in agreement with those obtained from ^1H NMR spectra.

Figure 1 shows the application of the composition data in Table I to linearization methods of the copolymer composition equation proposed by Kelen and Tüdös.³ Monomer reactivity ratios were determined according to the method of Kelen and Tüdös:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

with $\eta = G/\alpha + F$; $\xi = F/\alpha + F$

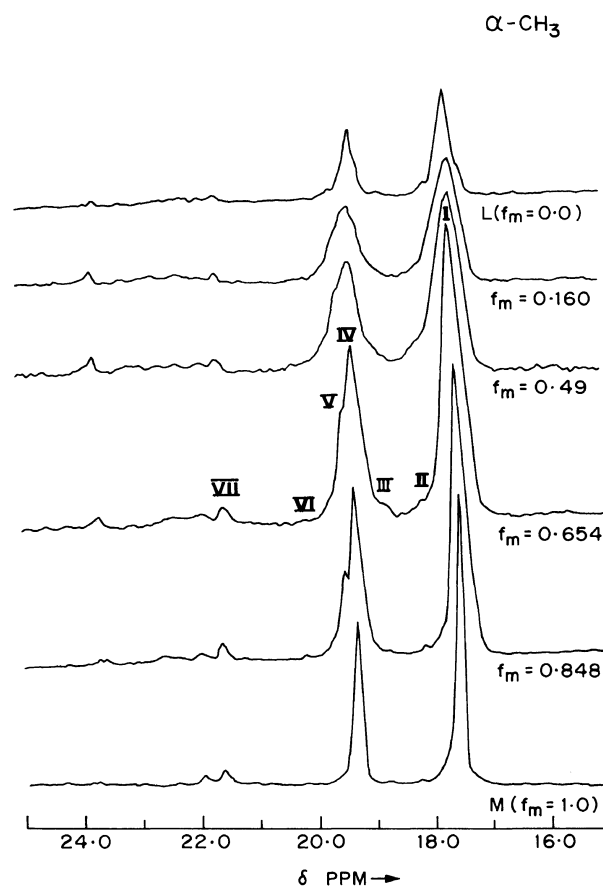
$$G = a - a/b; F = a^2/b$$

$$a = M_1/M_2 \text{ and } b = m_1/m_2$$

m_1, m_2 = mole fraction of monomers in the copolymer from ^1H NMR

M_1, M_2 = mole fraction of monomer in the feed

α is the geometric mean of the lowest and highest F . The plot of η vs. ξ is linear in Figure 1. From the slope and intersection with the ordinates r_1 and r_2 were determined as $r_1(\text{MMA}) = 1.38 \pm 0.11$ and $r_2(\text{LMA}) = 0.68 \pm 0.10$. In comparison, the reactivity of these two monomers when radically copolymerized in 1,1,2-trichloro-1,2,2-trifluoroethane at 60°C are $r_1(\text{MMA}) = 1.21 \pm 0.12$ and $r_2(\text{LMA}) = 0.84 \pm 0.10$.⁴ Agarwal *et al.*⁵ has reported


Figure 2. ^{13}C NMR spectra (75.5 MHz) of the $\alpha\text{-CH}_3$ side groups of M-L copolymers.

the reactivity ratio values of MMA and LMA as $r_1(\text{MMA}) = 0.45$ and $r_2(\text{LMA}) = 0.88$ in free radical bulk polymerization.

The microstructures and stereochemical configurations of copolymers prepared with different feed composition were determined from the exhaustive analysis of NMR resonance signals since the decoupled ^{13}C NMR spectra provide excellent and accurate information of the chemical composition and stereochemical configuration of copolymer chain segments. Statistical distributions of M- and L-centered sequences were determined from the conditional probabilities P_{ML} and P_{LM} (and $P_{MM} = 1 - P_{ML}$, $P_{LL} = 1 - P_{LM}$) (Table I). These values were calculated based on the classical terminal model for copolymerization.⁶ The parameters $P_{i,j}$ ($i, j = \text{M, L}$) are conditional probabilities for the addition of monomer units j to reactive i ends.⁷

The $\alpha\text{-CH}_3$ resonance of PLMA (Figure 2) shifted towards lower field compared to that of poly(methyl methacrylate) (PMMA) because of the long aliphatic character of the ester group in poly(lauryl methacrylate) (PLMA).

Effectively, the $\alpha\text{-CH}_3$ resonance of M and L units present a complex pattern with seven distinguishable peaks, whose intensities change with the average composition of copolymer samples (Figure 2). A detailed analysis of these signals leads to the assignment of peaks I and IV as due to the rr and $rm+mr$ triads in PPMA; in addition, the intensity of these signals increases with molar fraction of M in the copolymer. The expanded

^{13}C NMR decoupled spectra of the $\alpha\text{-CH}_3$ carbon resonance signals of homopolymers M and L as well as those of several M-L copolymer samples of various compositions are shown in Figure 2. The $\alpha\text{-CH}_3$ group is present in the chemical structure of both mesomeric units, but, for PMMA⁸ (M in Figure 2), this group gives three resonances at 17.58, 18.75, and 21.73 ppm from tetramethylsilane (TMS), assigned to iso (*mm*), hetero (*mr + rm*), and syndiotactic (*rr*) triads in order of increasing field.⁹

The $\alpha\text{-CH}_3$ group of PLMA also shows three resonance signals at 17.81, 19.45, and 21.61 ppm from TMS, assigned to *mm*, *mr + rm*, and *rr* tactic triads in order of increasing field, since these values are close to those reported for the resonance of the $\alpha\text{-CH}_3$ in PMMA.⁸⁻¹⁰

The (*rr*) and (*rm + mr*) resonances of PLMA (δ 17.81 and δ 19.45), appear in a somewhat lower field than those of the PMMA, (*rr*) at δ 17.58 and (*rm + mr*) at δ 18.50. However, the resonance signal assigned to isotactic (*mm*) sequences has an almost similar chemical shift for both the polymers (δ 21.60). This means that the $\alpha\text{-CH}_3$ side group in isotactic sequences shows very little sensitivity to the short chain and long chain aliphatic character of the ester groups. This is reasonable since the diamagnetic carbonyl centers are as far as possible from the $\alpha\text{-CH}_3$ group of the central unit in the triad (Figure 3). It is easily seen Figure 2 that the separation between tactic signals of PMMA is higher, $(\delta_{mm} - \delta_{mr}) \cong \delta_{mr} - \delta_{rr} \cong 1.71$ ppm, than that of PLMA $(\delta_{mm} - \delta_{mr}) \cong \delta_{mr} - \delta_{rr} \cong 1.54$ ppm. This means that except for (*mm*) sequences, the chemical shifts of M and L units are sensitive to the composition and the stereochemical configurations of the neighboring units in sequences of triads.

For a complete description of the monomer sequence distribution and relative stereochemical configuration in terms of M- and L-centered triads, it is necessary to take into consideration 10 different triads with a central M unit which may be magnetically distinguishable as is shown in the scheme of Figure 3. Similarly, 10 triads with a central L unit must also be considered. It is well known that the sensitivity of the $\alpha\text{-CH}_3$ resonance to tacticity arises from the diamagnetic effects of the carbonyl ester group of the neighboring units on the $\alpha\text{-CH}_3$ residue of the methacrylic central unit.²

Figure 3 as well as molecular models clearly show that the diamagnetic effects of neighboring units on the $\alpha\text{-CH}_3$ central unit for MML or LMM (*rr*) triads are different from those of MMA (*rr*) triads or LML (*rr*) triads and due to the difference in the chemical shifts (*rr*) sequences of both M and L homopolymers, it may be expected that the cosyndiotactic heterotriads or LMM (*rr*) give a resonance signal between those of the homopolymers. Therefore, we tentatively assign peak II to this kind of triad as indicated in Table II. Also, $\alpha\text{-CH}_3$ of central M unit of MML or LMM triads with the stereochemical configuration (*rr*) have the same magnetic and spatial arrangement as the MLL (*rr*) triads, so we have included these in signal II.

It thus may be expected that the LML (*rr*) sequence has the same chemical shift as the syndiotactic triad of homopolymer L and that the MLM (*rr*) is similar to the syndiotactic triad of homopolymer M (see Figure 3 and Table II).

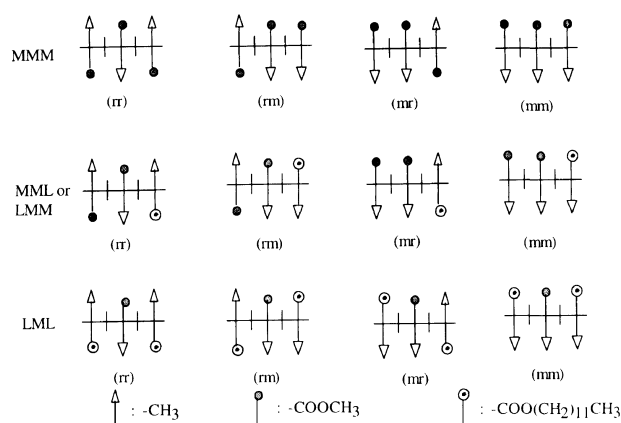


Figure 3. Schematic representation of M centered triads of methyl methacrylate-lauryl methacrylate copolymers.

Table II. Assignments of $\alpha\text{-CH}_3$ resonance to sequences of M- and L-centered triads^a

Spectral signal No.	Chemical shift/ppm	Copolymer compositions	Sequence configuration
I	17.46	MMM	<i>rr</i>
		MML	
II	18.10	MML	<i>rr</i>
		LMM	
		LLM	
III	18.63	LML	<i>rr</i>
		LLL	
IV	19.27	MMM	<i>mr + rm</i>
		MML	<i>rm</i>
		LMM	<i>mr</i>
		LML	<i>mr + rm</i>
V	19.83	MML	<i>mr</i>
		LMM	<i>rm</i>
		LLM	<i>mr</i>
VI	20.13	MLL	<i>rm</i>
		LMM	<i>mr + rm</i>
		LLM	<i>rm</i>
VII	21.50—21.90	a	<i>mm</i>

^a The signals considered in this interval correspond to all possible isotactic triads independent of composition.

Based on similar arguments we have assigned peak V to the contribution of sequences reported in Table II. The experimental data obtained from NMR spectra are in good agreement with the contribution of the corresponding sequences calculated statistically.

The molar concentrations of M- and L-centered sequences with statistical sequence distribution and stereochemical configuration of copolymer chains have been analyzed and correlated statistically according to the reactivity reported, the conditional probabilities P_{ij} quoted in Table I and average compositions of the copolymer samples. This analysis was carried out by making the following assumptions.

a) With respect to the chemical compositions of copolymer sequences, it is assumed that copolymerization reaction is described by the terminal unit model.^{11,12}

b) From a stereochemical point of view, it is assumed that the configurational sequence distribution may be described according to Bernoullian statistics with the isotactic parameters σ_{MM} , σ_{ML} , σ_{LM} and σ_{LL} as defined by Bovey¹³ and Coleman,¹⁴ where σ_{ij} is the probability of

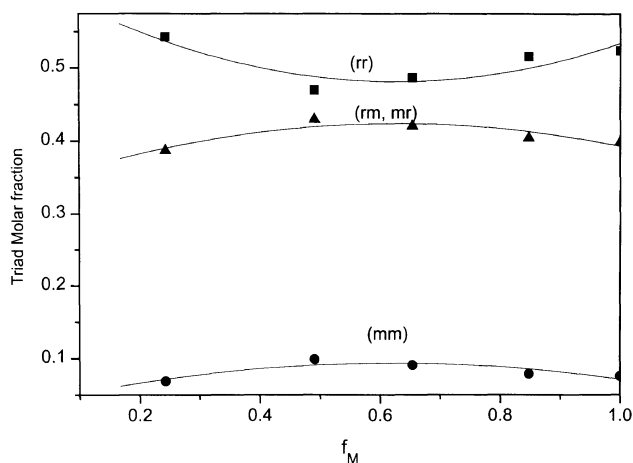


Figure 4. Variation in tactic sequences with M molar fraction in the copolymer. The points are experimental results from the $\alpha\text{-CH}_3$ resonance signals: $mm = \bullet$; $rm, mr = \blacktriangle$; $rr = \blacksquare$.

generating a *meso* diad between an *i* ending growing species and incoming *j* monomer.

$\sigma_{MM}=0.24$ and $\sigma_{LL}=0.27$ were considered for the statistical distribution of units in pure MMM and LLL triads. These values correspond to the isotacticity parameters of M and L homopolymers and were determined from the analysis of the $\alpha\text{-CH}_3$ resonances of PMMA and PLMA, considering the Bernoullian distribution of tactic sequences. The coisotacticity parameters σ_{ML} and σ_{LM} are not accessible directly, but it is reasonable to assume that $\sigma_{ML} = \sigma_{LM} = \sigma^*$.^{15,16} In this way we determined this parameter by comparison of the integrated intensities of peak I & II of the $\alpha\text{-CH}_3$ resonances (assigned as indicated in Table II) for several copolymer samples. Application of well known statistical relations¹⁷ gives a value of $\sigma_{ML} = \sigma_{LM} = 0.30$.

Figure 4 shows variation in the concentrations of tactic sequences (independently, their chemical composition), with average molar fraction M in the copolymer chain. It clearly shows that there is a slight increase of the coheterotactic sequences with molar fraction of M in the copolymer samples, but, in any case, from a stereochemical point of view one can conclude that there is a random distribution to tacticity following the classical Bernoullian triad.

Carbonyl Carbon Resonance Signals

We examined the validity of the statistical model, from analysis of the complex pattern of the carbonyl carbon resonance signals. Figure 5 shows the spectra of the C=O resonances for four copolymer samples of different composition, together with those of corresponding M and L homopolymers. The calculated and observed peak intensities are compared in Tables III and IV for PMMA and PLMA respectively. They agree well with each other indicating that pentad distributions in the samples obey Bernoullian statistics. The C=O resonance of PLMA reveals that this group presents a resonance pattern very similar to that of PMMA. The assignment of PLMA was carried out in terms of tactic pentads in the same manner as for PMMA.^{9,10}

The spectra of copolymers (Figure 5) when compared with those of homopolymers M and L reveal that some peaks overlap with each other, but with intensities ac-

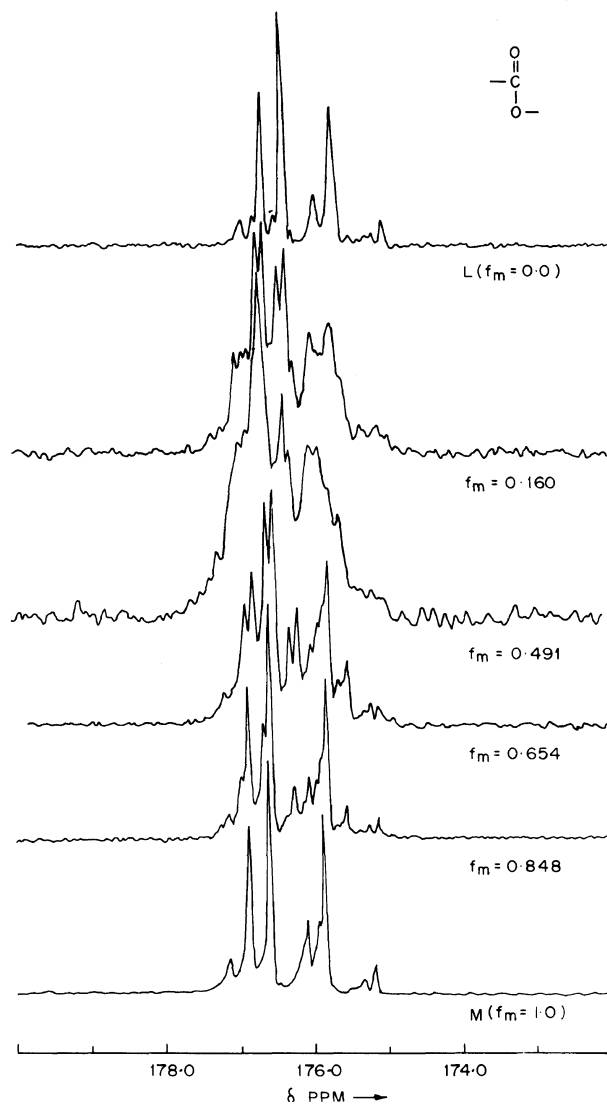


Figure 5. ^{13}C NMR spectra (75.5 MHz) of the C=O side groups of M-L copolymers.

Table III. Experimental and calculated pentad probabilities for poly(methyl methacrylate) samples using GTP

^{13}C	C=O	Pentads	ppm	Observed	Calculated
		<i>mrrm</i>	177.12	0.044	0.039
		<i>mrrr</i>	176.86	0.204	0.209
		<i>rrrr</i>	176.59	0.277	0.276
		<i>rmrm</i>	176.46	0.084	0.080
		<i>mmrr</i>	176.09	0.089	0.080
		<i>rmrr</i>	175.94	0.216	0.210
		<i>mmrm</i>	175.85	0.015	0.030
		<i>mmmr</i>	175.71	0.014	0.030
		<i>rmnr</i>	175.46	0.020	0.006
		<i>mmmm</i>	175.32	0.035	0.039

Calculation based on intensity of C=O group. P_m calculated from intensity of *mm* triad of $\alpha\text{-CH}_3$ group of PMMA.

ording to the average molar composition of copolymer chains. This means that the C=O resonances of M and L-centered sequences are not sensitive to the chemical composition and distribution of monomeric units but are sensitive to the relative stereochemical configuration of copolymer segments in terms of sequences of tactic pentads. This assignment is similar to that of the $>\text{C}=\text{O}$

Table IV. Experimental and calculated pentad probabilities for poly(lauryl methacrylate) samples using GTP

¹³ C	C=O	Pentads	ppm	Observed	Calculated
		<i>mrrm</i>	177.0	0.036	0.040
		<i>mrrr</i>	176.77	0.205	0.209
		<i>rrrr</i>	176.49	0.283	0.273
		<i>rmrm</i>	176.32	0.089	0.080
		<i>mmrr</i>	176.01	0.068	0.031
		<i>rmrr</i>	175.78	0.188	0.209
		<i>mrrm</i>	175.55	0.058	0.080
		<i>mmmr</i>	175.29	0.014	0.028
		<i>rmmr</i>	175.23	0.020	0.010
		<i>mmmm</i>	175.10	0.037	0.040

Calculation based on intensity of C=O group. P_m calculated from intensity of *mm* triad of α -CH₃ group of PLMA.

Table V. Stereochemical configurations of M-centered pentads determined from analysis of C=O resonance signals

Tactic pentad	Chemical shift/ppm	f_M (Copolymer)			
		0.243	0.491	0.654	0.848
<i>mrrm</i>	177.33	0.030	—	0.011	0.021
<i>mrrr</i>	177.21	0.037	0.099	0.038	0.038
<i>rrrr</i>	176.88	0.138	0.268	0.176	0.211
<i>rmrm</i>	176.59	0.148	—	0.276	0.344
<i>mmrr</i>	176.00	0.159	—	0.094	0.090
<i>rmrr</i>	175.96	0.139	0.244	0.119	0.085
<i>mrrm</i>	175.90	0.133	0.243	0.139	0.119
<i>mmmr</i>	175.71	0.174	—	0.054	0.021
<i>rmmr</i>	175.59	—	0.145	0.074	0.047
<i>mmmm</i>	175.33	0.041	—	0.019	0.014

Table VI. Stereochemical configurations of L-centered pentads determined from analysis of C=O resonance signals

Tactic pentad	Chemical shift/ppm	f_L (Copolymer)			
		0.152	0.346	0.509	0.757
<i>mrrm</i>	177.00	0.116	0.118	0.151	0.111
<i>mrrr</i>	176.63	0.208	0.218	0.295	0.250
<i>rrrr</i>	176.49	0.044	0.232	—	0.203
<i>rmrm</i>	176.25	0.097	0.095	0.143	0.103
<i>mmrr</i>	176.00	0.113	0.074	0.148	0.131
<i>rmrr</i>	175.83	0.302	0.159	0.146	0.110
<i>mrrm</i>	175.55	0.059	0.062	0.088	—
<i>mmmr</i>	175.38	0.018	0.010	0.028	0.034
<i>rmmr</i>	175.13	0.042	0.019	—	0.033
<i>mmmm</i>	174.95	—	0.008	—	0.025

resonance signals for PMMA and PLMA homopolymers and reported by Yamakawa *et al.*¹⁸ The chemical shifts of signals assigned to tactic pentads centered in M units, together with the molar fraction of sequences for copolymers with different average molar fraction of M, are listed in Tables V and VI lists the corresponding values for L-centered sequences. In this case, overlapping between 177.50 and 175.00 ppm with more intense syndiotactic L-centered sequences (see Figure 5) and also permit us to determine the contribution of isotactic M centered sequences. Therefore, the values in Table VI for these sequences were calculated statistically according to the model described before; nevertheless, their contribution to the whole system can be disregarded in practice.

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