Nucleophilic Substitution onto Poly(methyl methacrylate). 5. Synthesis and Characterization of Some Tautomerizable Heterocyclic Copolymers

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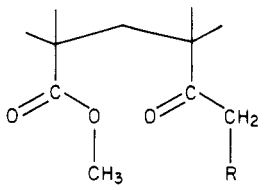
ABSTRACT: The reaction of a series of heterocyclic organolithium reagents ($HetCH_2Li$) onto radical or stereoregular poly(methyl methacrylate) (PMMA) in homogeneous solution (tetrahydrofuran, benzene + hexamethylphosphoramide) is investigated as a general route to functionalize polymeric chains with tautomerizable keto-β-heterocyclic structures. The systems essentially involve 2-picolinyl- and quinaldinyllithium (20 °C) and [(4,4-dimethyl-2-oxazol-2-yl)methyl]lithium and [2-thiazol-2-ylmethyl]lithium (−15 °C). Copolymer characterization (UV and ^1H NMR spectroscopy, potentiometry, molecular weight measurements, cross fractionation) shows that nucleophilic substitution on the ester function occurs selectively without any side reaction and leads to the controlled introduction of the $COCH_2Het$ group in the PMMA chain; the substitution degree depends on the thermal stability of the organolithium reagent and may be easily monitored by the initial stoichiometric ratio $[Het\text{-}CH_2Li]_0/[ester]_0$ within a fairly wide composition range. In dilute aprotic solution, the copolymers show specific tautomeric equilibria: ketone ⇔ chelated enol for keto-2-picolinyl structures and ketone ⇔ chelated enamine for ketoquinaldinyl and keto-β-oxazolyl structures, with a characteristic shift toward the conjugated tautomer and a strong decrease of the sensitivity to solvent polarity effects with respect to the model compounds $(CH_3)_3CCOCH_2Het$.

Introduction

A few years ago we presented a survey of nucleophilic substitution of primary organolithium reagents RCH_2Li stabilized by sulfur groups onto poly(methyl methacrylate) (PMMA) leading to copolymers bearing keto-β-functionalized units (B units, $COCH_2R$)[1]

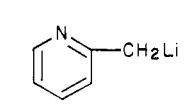


A B

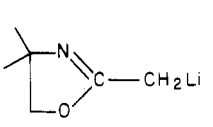
R = SC_6H_5, SO_xCH_3 (with $x = 1, 2$), $SO_2N(CH_3)_2$

These copolymers show well-defined and easy to control molecular characteristics, such as the same $\overline{DP}_n$ and tacticity as the PMMA precursor and high compositional homogeneity,[2] and the molar substitution degree ($\overline{DS}_m$) was merely monitored by the initial stoichiometric ratio $[RCH_2Li]_0/[ester]_0$ within a wide composition range ($\overline{DS}_m < 0.6$).

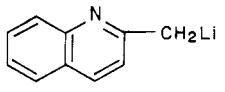
In the present work we extend our experiments to four homologous primary organolithium reagents stabilized by heterocyclic rings, $HetCH_2Li$



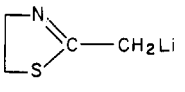
2-picolinyllithium[3,4]



[(4,4-dimethyl-2-oxazol-2-yl)methyl]lithium[5,6]

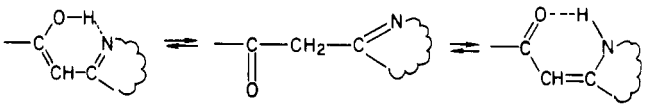


quinaldinyllithium[3,4]



[2-thiazo-2-ylmethyl]lithium[5,6]

The major goal of our studies is to perform a comprehensive analysis of the reaction process as a general and versatile strategy to functionalize PMMA and its copolymers with tautomerizable keto-β-heterocyclic moieties, $COCH_2Het$, that show prototropic equilibrium between the ketonic and conjugated enol or enamine structures



chelated enol ketone chelated enamine

This characteristic tautomerism[7] is of special interest from at least two complementary viewpoints: (i) the critical comparison of prototropic equilibria on well-defined macromolecular chains and on their homologous model compounds $(CH_3)_3CCOCH_2Het$ (to our knowledge, reliable data on this topic are rather scarce and restricted to polymeric 1,3-dicarbonyl compounds[8,9]); (ii) the study of the specific properties of the enolic or enaminic forms, ranging from transition-metal complexation[10] to bacteriostatic activity.[11] Moreover, the involved reaction may probably be considered in a first approach as a model for the anionic grafting of living poly(vinyl heterocyclic) chains onto PMMA.

Part of our results has already been briefly published,[12] and this paper is devoted to a full report on the synthesis and characterization of the functionalized PMMA and to a short survey of their specific tautomerism.

Results

It is long known[3-6] that nucleophilic substitution of the selected heterocyclic organolithium reagents on monofunctional low molecular weight esters RCO_2R' readily leads to the keto-β-heterocycles $RCOCH_2Het$. Moreover our previous studies[1] suggested that this process should be directly transposed to atactic and stereoregular PMMA. All the reactions were carried out in homogeneous solution in the presence of hexamethylphosphoramide (HMPA) within a temperature range compatible with the organolithium reagent stability and for various initial stoichiometric ratios $[HetCH_2Li]_0/[ester]_0$ (see further and Experimental Section). As in the preceding work,[1] structural analysis of the derived copolymers was performed by combining elemental analysis, spectroscopic (IR, UV, ^1H NMR) measurements, and potentiometric measurements, using systematically model compounds $(CH_3)_3CCOCH_2Het$ as references for every analytical method. In the following text, the copolymer name is related to the tacticity of its precursor and to the nature of the heterocyclic nucleus:

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Table I
Characteristic Chemical Shifts (δ) (±0.02) of the Various Tautomers of Keto-β-heterocyclic Structures in Semidilute Solution[a]

H atoms	keto-2-picolines, Me_2SO, 70 °C		ketoquinaldines, Me_2SO, 70 °C		keto-β-oxazolines, $CDCl_3$, 50 °C	
	model 1	SP-2	model 2	SQ-1	model 3	RO-3
O=CCH$_2$Het	4.02 s	4.11 s	4.20 m	4.20 bs	4.04 s	
OC=CHHet	5.44 s	5.44 s				
O=CCH=Het			5.57 d	5.58 bs	5.04 s	5.00 d
H_6 enol	8.22 d	8.24 d				
H_6 ketone	8.38 d	8.44 d				
H_3 enamine			6.95 m	6.88 bs		
H_4 ketone			8.25 m	8.15 bs		
OH···N=C	15.00 bs	15.10 bs				
NH···O=C			15.10 bs	14.90 bs	9.66 bs	9.52 bs

[a] Solution is 3–6% (w/v). $\overline{DS}_m$ = 0.298, 0.223, and 0.360 for SP-2, SQ-1, and RO-3, respectively. s, singlet; bs, broad singlet; d, doublet; m, multiplet.

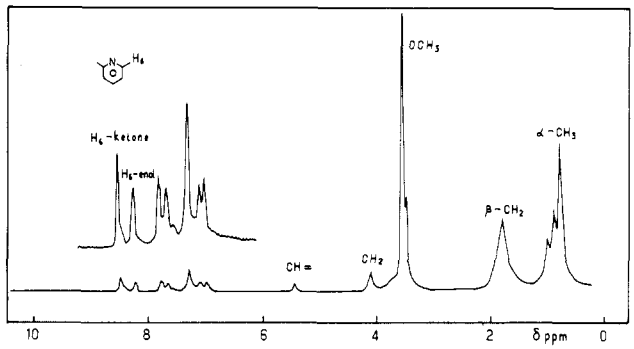


Figure 1. ^{1}H NMR spectrum of SP-2 copolymer ($\overline{DS}_m$ = 0.298) in 3% solution in Me_2SO-d_6 at 70 °C.

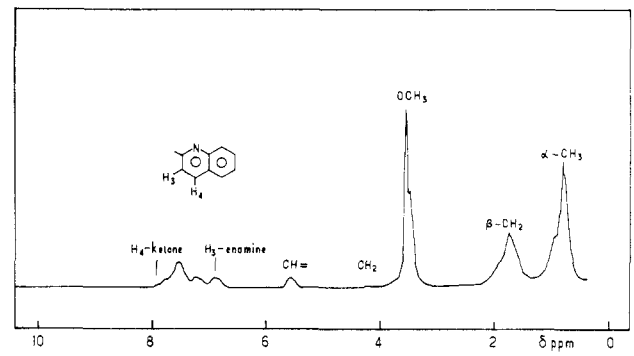


Figure 2. ^{1}H NMR spectrum of SQ-1 copolymer ($\overline{DS}_m$ = 0.223) in 3% solution in Me_2SO-d_6 at 70 °C.

RP, radical PMMA substituted by picolinyl units and SO, syndiotactic PMMA substituted by oxazolyl units, for instance. $\overline{DS}_m$ and $\overline{DS}_w$ are the molar and weight substitution degrees, respectively; A and B are the original MMA and the substituted units, respectively.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR spectra of the copolymers obtained at 250 MHz in various solvents (Me_2SO-d_6, $CDCl_3$) are generally well resolved enough to allow the determination of composition and of the fraction of the various tautomers: three representative spectra are given in Figures 1–3. For the derivation of reliable composition data we avoided taking into account the resonance pattern of the acidic $COCH_2Het$ methylenic hydrogen atoms, which may be prone to H–D isotopic exchange with the solvent (actually observed in CD_3COCD_3 solution). Combination of the integrated intensities of the peaks related to the α-CH_3 and β-CH_2 backbone, to the residual OCH_3 ester units, and to the specific heterocyclic hydrogen atoms directly leads to the $\overline{DS}_m$ values.

In the nonaromatic solvents used, the ester OCH_3 resonance pattern is insensitive to tacticity effects, and the weak splitting observed for most copolymers probably arises from neighboring group effects within the three distinct triads AAA AAB and BAB. The more complex pattern of the backbone CH_3 reflects both configurational and compositional effects. In the easier case of stereoregular picolinyl copolymers, where tacticity influence is obviously cancelled, the pattern involves six theoretically distinct A- or B-centered triads; it actually appears as a wide and poorly resolved multiplet for isotactic chains (δ = 1.49 in pyridine-d_5). For syndiotactic copolymers however it is split into a fairly well-defined doublet in pyridine (δ = 1.22 and 1.40) or triplet in Me_2SO (see Figure 1). The analysis of unit distribution along the chain is out of the scope of the present work.

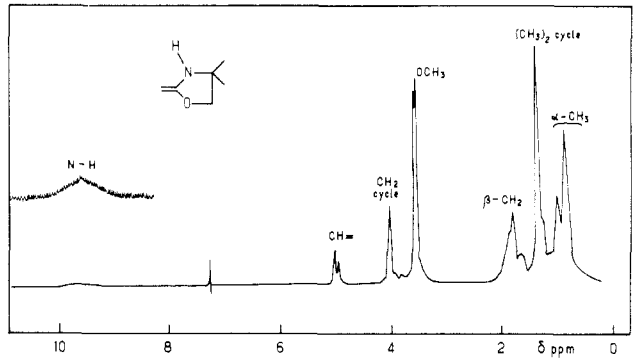


Figure 3. ^{1}H NMR spectrum of RO-3 copolymer ($\overline{DS}_m$ = 0.360) in 5% solution in $CDCl_3$ at 20 °C.

The identification and quantitative determination of the different tautomers in equilibrium in solution rest upon well-ascertained ^{1}H NMR literature data for low molecular weight keto-2-picolines,[13-15] ketoquinaldines,[13,16] and keto-β-oxazolines.[5] The hydrogen atoms of interest are outlined in Scheme I, and their specific chemical shifts measured in semidilute solution are collected in Table I, with special emphasis on the aromatic patterns for picolinyl and quinaldinyl structures that allow the most accurate measurements of the ketonic and conjugated tautomer fractions. Solvent nature, copolymer composition, and temperature may induce some weak variations in the δ values or in the peak shape without modifying the overall spectrum analysis: for instance, at 30 °C for RP copolymers, $\delta(COCH_2Pyr)$ is independent of chain composition and increases from 4.07 to 4.42 when going from $CHCl_3$ to pyridine solution (hydrogen bonding in the latter case), while δ(CH=Pyr) in pyridine solution slightly decreases with increasing $\overline{DS}_m$ from 5.77 ($\overline{DS}_m$ = 0.123) to 5.59 ($\overline{DS}_m$ = 0.615), with respect to 5.55 for the model

Scheme I

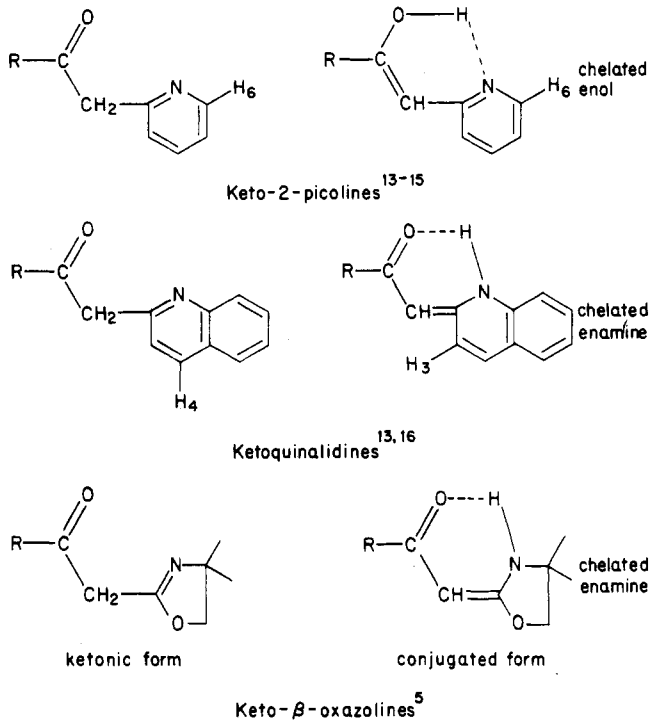


Table II
UV Transition of the Various Chromophores in CF_3CO_2H Solution

heterocycle	sample	λ_{max}, nm	ϵ, L mol^{-1} cm^{-1}
keto-2-picoline	model 1	263	7500
	copolymers	263	7700
ketoquinaldine	model 2	319	10400
	copolymers	319	10100
keto-β-oxazoline	model 3	264	1700
	copolymers	268–286[a]	2250

[a] λ_{max} increases from 268 to 286 nm when increasing $\overline{DS}_m$ from 0.217 to 0.627.

compound.

UV Spectroscopy. In strong carboxylic acid solvents, such as formic or trifluoroacetic acids, the tautomeric equilibria of B units are quantitatively shifted toward the protonated ketonic forms.[13] Under these conditions the UV spectra of both copolymers and model compounds are characterized by a single well-defined absorption band related to the $\pi \rightarrow \pi^*$ transition of the protonated heterocycle which shows no deviation from Beer's law: see Table II. If the UV absorption of copolymers depends only on the total concentration of the chromophores, the optical densities D and composition $\overline{DS}_w$ data (determined independently as discussed below) must be related through the simple relationship

$$D\mathcal{M}_B/cl = \epsilon_{cop}\overline{DS}_w$$

where $\mathcal{M}_B$ is the molecular weight of the substituted B unit, c the weight concentration of the solution, and ϵ_{cop} the molar absorptivity per chromophore in the copolymer chain. The experimental results given in Figure 4 and Table II lead to the following conclusions: (i) In all cases, ϵ_{cop} is independent of copolymer microstructure (tacticity and unit distribution). (ii) $\pi \rightarrow \pi^*$ transitions are nearly identical for picolinyl and quinaldinyl copolymers with respect to their model compounds. (iii) When compared to its low molecular weight homologue, oxazolyl copolymers show a definite hyperchromicity and an hypsochromic shift

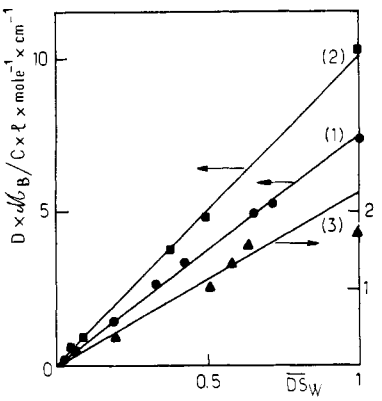


Figure 4. UV data for various models and copolymers in their protonated ketonic form in CF_3CO_2H solution: (●) picolinyl, (■) quinaldinyl, and (▲) oxazolyl structures.

Table III
Acid–Base Potentiometric Titration of the RO Copolymers: Fraction F of Titrable Keto-β-oxazolyl Units

Acidity Measurements: CH_3ONa/CH_3OH–DMF

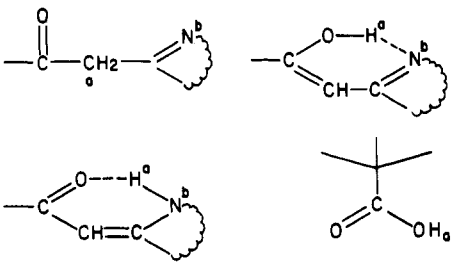
sample	model	RO-1	RO-2	RO-3	RO-4	RO-5
$\overline{DS}_m$	3	0.133	0.300	0.360	0.428	0.482
F	1	0.834	0.950	0.867	0.783	0.720

Basicity Measurements on RO-4: $HClO_4/CH_3CO_2H$

solv, pK_a (H_2O)	CF_3CH_2OH (12.4)	CH_3CO_2H (4.7)	$HSCH_2CO_2H$ (3.6)	Cl_2CHCO_2H (1.3)
F	0.797	0.811	0.790	0.934

which increases with the B unit content.

Acid–Base Potentiometric Measurements. The various copolymers show a number of acid (site a) or basic (site b) functions of rather differentiated strengths provided by the B units or carboxylic acid groups arising from side reactions (see further discussion).



We succeeded in performing a series of potentiometric measurements using various solvent-titrating reagent systems and taking into account the behavior of the various model compounds.

Tetrabutylammonium hydroxide in MeOH–i-PrOH allows the quantitative and exclusive determination of the carboxylic acid units in dimethylformamide (DMF) solution. They may be quantitatively and selectively methylated by diazomethane in the absence of any catalyst.[17]

Sodium methoxide in C_6H_6–CH_3OH shows a complex behavior. In DMF solution, for keto-β-oxazolyl structures, the model affords one acid equivalent, while only a fraction of the same units is actually titrated on copolymers: see Table III.

Keto-2-picolinyl functions behave in a similar way, while ketoquinaldinyl structures do not afford any clear equivalence point. It would be tempting to correlate tentatively the measured acidity with the enolization extent of the various samples in the ternary medium C_6H_6–CH_3OH–DMF, but our limited experimental results do not allow us to check this apparently reasonable assumption.[18]

Table IV
Comparison of the $\overline{DS}_m$ Values Derived from the Various Analytical Methods

run	elem anal.	^{1}H NMR	basicity[a]	acidity[b]
RP-1	0.119 ± 0.002	0.126 ± 0.006	0.121 ± 0.002	0.117 ± 0.002
RP-3	0.561 ± 0.011	0.558 ± 0.028	0.539 ± 0.011	0.533 ± 0.011
SQ-1	0.235 ± 0.005	0.220 ± 0.011	0.211 ± 0.004	
RO-1	0.133 ± 0.003	0.139 ± 0.007		0.146 ± 0.003
RO-4	0.428 ± 0.008	0.413 ± 0.021		0.428 ± 0.008

[a] Titration by $HClO_4$ in CH_3CO_2H solution. [b] Titration by $(CH_3)_3COK$ in THF solution, after previous methylation of carboxylic acid units, if necessary.

Table V
Fractionation of Copolymer RO-2 ($\overline{DS}_m$ = 0.300)[a]

method	yield %	$\overline{DS}_m$	$\bar{\sigma}^2 \times 10^4$	V
single-step fract (system I)	93	0.302	1.01	1.19
cryss fract (systems I + II)	90	0.298	5.60	1.50

[a] $\bar{\sigma}^2 = \sum_i w_i(DS_m^i - \overline{DS}_m)^2$. $V = u^+/u^-$, where $u^+ = \sum_i w_i(DS_m^i - \overline{DS}_m)$, with $DS_m^i > \overline{DS}_m$ and $u^- = \sum_j w_j(\overline{DS}_m - DS_m^j)$, with $DS_m^j < \overline{DS}_m$.

Potassium tertiobutylate in tetrahydrofuran (THF) solution readily leads to a quantitative titration of all the keto-β-heterocycles under study, on polymers as well as on model compounds. This feature is in good agreement with the high basicity of the aprotic system $(CH_3)_3COK$–THF.[19] Transesterification of A ester units does not occur at all in the potentiometric titration conditions.

Anhydrous perchloric acid in acetic acid solution allows a quantitative titration of all the investigated heterocycles except that of keto-2-oxazolyl structures. In the latter case, the fraction of the titrated B units apparently decreases with the strength of the acidic solvent (increasing pK_a): see Table III. This failure may arise from side reactions such as cationic opening of the oxazolyl ring in presence of very strong acids.[20]

The good agreement generally observed between the experimental $\overline{DS}_m$ values derived from elemental analysis (±2%), ^{1}H NMR (±5%) spectroscopy, and acid–base potentiometric (±2%) measurements is outlined for some representative copolymers in Table IV.

Copolymer "Cross" Fractionation. Compositional homogeneity of a representative copolymer sample RO-2 ($\overline{DS}_m$ = 0.300, $\bar{M}_n = 8.58 \times 10^4$) was analyzed by "cross" fractionation, which has been critically discussed and definitely shown to be of greater efficiency for copolymers showing only slight fluctuations in composition.[2] In Figure 5 are plotted the nearly linear variations (slope λ) of the first cloud points γ_1 at room temperature in various ternary systems copolymer–solvent–nonsolvent vs. the $\overline{DS}_m$ values for RO copolymers of similar molecular weights ($\bar{M}_n$ increases from 7×10^4 for PMMA to 9.6×10^4 for RO-5 copolymer of $\overline{DS}_m$ = 0.482).

"Cross" fractionation involves the two solvent–nonsolvent systems characterized by the highest λ values of opposite signs:[2] first, rough fractionation of the RO-2 copolymer in chloroform–*n*-hexane (system 1) and then refractionation of every primary fraction in acetonitrile–water (system 2). The composition distribution curves are given in Figure 6, and the experimental results analyzed in terms of the variance $\bar{\sigma}^2$ and of the distribution symmetry V[21] are compared in Table V. "Cross" fractionation is much more efficient than the single-step procedure and shows a dissymmetric unimodal distribution. The accuracy on DS_m^i value for every fraction (about 2%) yields an apparent compositional distribution characterized by a $\bar{\sigma}^2$ value of about 4×10^{-5} for a perfectly homogeneous copolymer. The higher value actually measured, $\bar{\sigma}^2 = 5.6 \times 10^{-4}$, is thus significant of a weak but well-ascertained compositional heterogeneity.

Table VI
Molecular Weights of Some Representative Substituted PMMA

run	$\overline{DS}_m$	dn/dc,[a] mL g^{-1}	$\bar{M}_w \times 10^{-5}$ calcd[b]	$\bar{M}_w \times 10^{-5}$ exptl	$\bar{M}_n \times 10^{-4}$ calcd[b]	$\bar{M}_n \times 10^{-4}$ exptl
RP-1	0.123	0.084	1.04	0.97		
RP-2	0.313	0.110	1.16	1.06		
RP-4	0.615	0.148	1.34	1.17		
RO-1	0.133				7.64	8.20
RO-3	0.360				8.91	9.37

[a] As expected, the dn/dc values measured in DMF solution at room temperature for λ 5460 Å are a linear function of $\overline{DS}_w$. [b] $\bar{M}_{calcd} = \overline{DP}^0[\mathcal{M}_A(1 - \overline{DS}_m) + \mathcal{M}_B\overline{DS}_m]$, where $\overline{DP}^0$ is the weight- or number-average degree of polymerization of the PMMA precursor and $\mathcal{M}_A$ and $\mathcal{M}_B$ are the molar mass of the A and B units, respectively.

Table VII
Reaction of 2-Picolinyl- and Quinaldinyllithium onto PMMA at 25 °C in Homogeneous THF–HMPA Solution

run	$[HetCH_2Li]_0/[ester]_0$	time, h	$\overline{DS}_m$	yield,[b] %
RP-1	0.30	2	0.123	82.0
IP-1	0.30	4	0.095	63.3[c]
SP-1	0.60	4	0.233	77.7[c]
SP-2	0.60	24	0.298	99.3
RP-2	0.65	6	0.313	96.3
IP-2	0.65	20	0.312	96.0
IP-3	0.70	4	0.239	68.3[c]
RP-3	1.20	24	0.583	89.7
RP-4	2.00	12	0.615	61.5
SQ-1	0.60	24	0.223	74.3
IQ-1	0.65	20	0.321	98.8
RQ-1	1.00	24	0.419	83.8

[a] THF–HMPA 2:1 (v/v) solution; [PMMA] = 0.4 mol L^{-1}. [b] Yield % = $100 \times 2 \times \overline{DS}_m \times [ester]_0/[HetCH_2Li]_0$. [c] PMMA precursor of high molecular weight $\bar{M}_w > 4 \times 10^5$; the whole reaction medium appears as an homogeneous gel at the end of the reaction process.

Table VIII
Reaction of [(4,4-Dimethyl-2-oxazol-2-yl)methyl]lithium and of (2-Thiazol-2-ylmethyl)lithium onto PMMA in Homogeneous THF–C_6H_6–PMMA Solution[a]

run[b]	$[HetCH_2Li]_0/[ester]_0$	t, °C	time, h	$\overline{DS}_m$	yield, %
RO-1	0.30	20	2.5	0.133	88.7
RO-2	0.62	−15	4	0.300	96.8
RO-3	0.90	20	4	0.360	80.0
RO-4	2.00	−15	18	0.428	42.8
RO-5	4.00	−15	28	0.482	48.2
RT-1	0.90	−15	4.5	0.060	13.3
RT-2	0.90	−15	24	0.101	22.4
RT-3	0.90	20	24	0.140	31.1

[a] THF–C_6H_6–PMMA 4:2:1 (by vol) solution; [PMMA] = 0.2 mol L^{-1}. [b] All the reactions are initially carried out at −70 °C for 1.5 h, and then at a higher temperature for a given time, as quoted in the table.

Molecular Weight Measurements. The fluctuations in composition of the copolymers are low enough so that light scattering measurements lead to apparent $\bar{M}_w$ values quite close to the actual weight-average molecular weights.[2] Some representative data are given in Table VI.

Discussion

Synthetic and Mechanistic Features of Nucleophilic Substitution of $HetCH_2Li$ onto PMMA. The

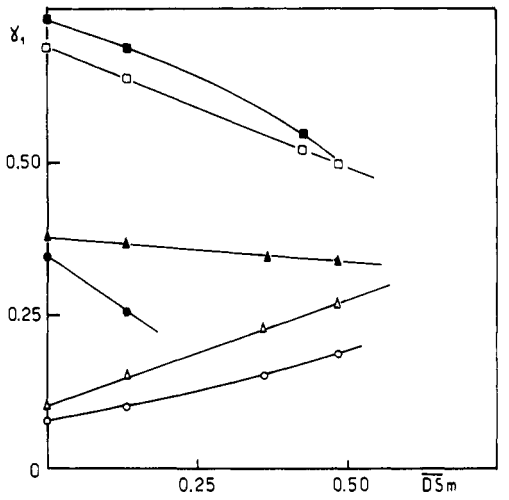


Figure 5. Variations of the first cloud point (volume fraction of the nonsolvent in the medium) with copolymer composition for various ternary systems RO copolymers–solvent–nonsolvent at 20 °C: (■) $CHCl_3$–Et_2O; (□) $CHCl_3$–hexane; (▲) CH_3COCH_3–hexane; (△) CH_3CN–H_2O; (●) C_6H_6–hexane; (○) DMF–H_2O.

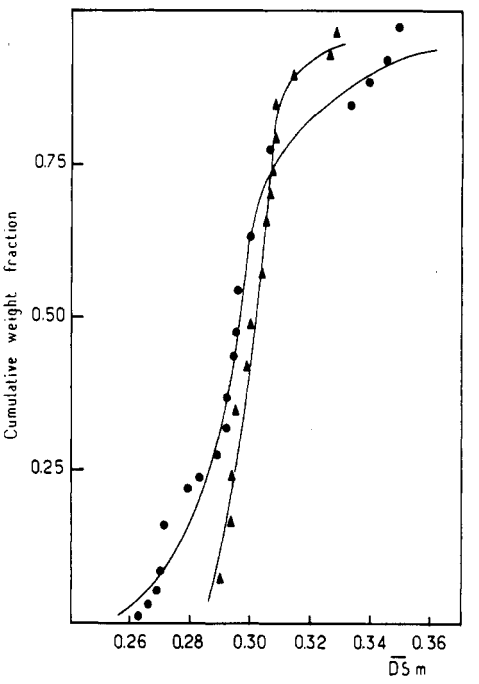
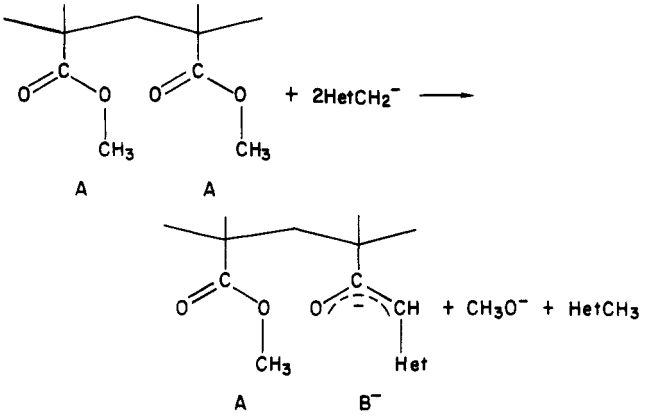


Figure 6. Compositional distribution of RO-2 copolymer ($\overline{DS}_m$ = 0.300): (▲) single-step fractionation ($CHCl_3$–hexane); (●) cross fractionation ($CHCl_3$–hexane and then CH_3CN–H_2O).

experimental results collected in Tables VII and VIII may be readily discussed all together within the general framework previously developed for similar systems.[1]

(a) As for low molecular weight monofunctional esters,[3-6] the reaction process leads to the keto-β-heterocycle in its enolate form B^- in the reaction medium according to the following scheme:



As previously shown[1] the possible intramolecular cyclization reactions within AB^- or B^-B^- diads, leading to cyclic β-diketones and cyclic α,β unsaturated ketones, respectively, probably do not occur to any appreciable extent in the aprotic reaction medium for temperatures below 25 °C: besides the good self-consistency of the compositional data derived from the various methods assuming a simple binary A_xB_y structure for the copolymer, we were unable to get any clear spectroscopic evidence for such conjugated structures.

(b) The *o*-alkyl scission of the ester group, leading to methacrylic acid units, arises from increasing steric hindrance around the carbonyl function as the substitution proceeds further.[1] It is actually observed only for RP copolymers of $\overline{DS}_m \geq 0.30$ and to a very low level: a molar fraction of carboxylic acid units of 0.003, 0.017, and 0.027 for $\overline{DS}_m$ of 0.313, 0.538, and 0.615, respectively.

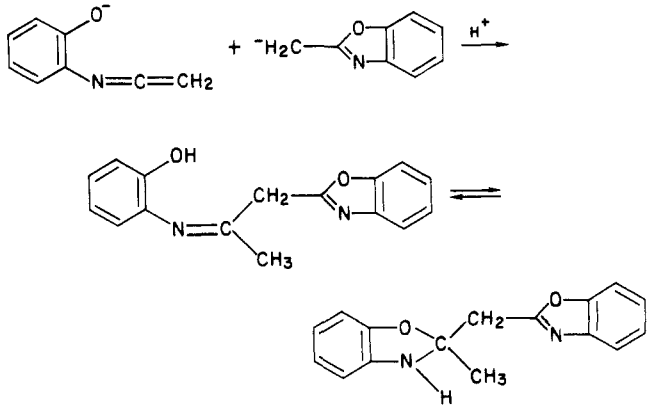
(c) The good agreement between experimental and calculated $\bar{M}_w$ or $\bar{M}_n$ values (Table VI) points out the lack of any significant degradation or cross-linking side reaction. The gelled reaction medium sometimes observed, especially with high molecular weight PMMA (see Table VII), arises from intermolecular association of the organolithium chains which is disrupted upon acidification.

The main feature of the reaction process arises from the increasing anionic character of the copolymer chain $A_xB_y^-$ as the substitution proceeds further: this restricts its solubility in the reaction medium to strongly dipolar aprotic solvents, such as HMPA for $\overline{DS}_m > 0.20$, and determines the overall kinetics and thus the copolymer microstructure (A and B unit distribution and compositional homogeneity).

Because of increasing steric hindrance and electrostatic field effects and by analogy with the very homologous organolithium–PMMA systems previously analyzed,[1,12] the reaction might be characterized by autoretarded kinetics (especially for syndiotactic chains) described in terms of neighboring group effects within the three kinds of triads

$$k_0(A\breve{A}A) \geq k_1(A\breve{A}B^-) \gg k_2(B^-\breve{A}B^-)$$

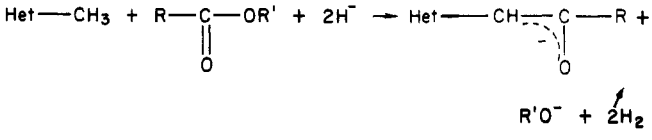
In spite of very high or even quantitative yields for low or moderate $\overline{DS}_m$ (see tables VII and VIII) the autoretarded kinetics may imply some characteristic limiting conversions: (i) $k_2(B^-\breve{A}B^-) = 0 \rightarrow \overline{DS}_{m,max} = 0.666$[22,23] (this is typical for the 2-picolinyllithium/R-PMMA at room temperature ($\overline{DS}_{m,max} \simeq 0.615$), as previously observed for most of the sulfur-stabilized organolithium reagents[1]); (ii) $k_1(B^-\breve{A}A) = k_2(B^-\breve{A}B^-) = 0 \rightarrow \overline{DS}_{m,max} = 0.432$[22,23] (this could be the case of the [oxazol-2-ylmethyl]lithium at −15 °C ($\overline{DS}_{m,max} \simeq 0.43$–$0.48$), but this very low reactivity of the chain cannot be definitely ascertained since dimerization (especially for $T > 0$ °C) of the lithium reagent[5] can compete with the desired substitution). The thermal instability of the reagent is even more critical for [thiazol-2-ylmethyllithium][6] ($\overline{DS}_{m,max} \simeq 0.14$). Finally, no reaction occurs between [benzoxazol-2-ylmethyl]lithium and PMMA within the temperature range −70 to 0 °C, where only the dimer (see Experimental Section), arising probably from a similar condensation involving rearrangement of the carbanion into its ketimine form, was isolated and identified.[5]



As a consequence of autoretarded kinetics[22,23] and by analogy with the [(methylsulfonyl)methyl]lithium/PMMA system previously analyzed[12] (k_0:k_1:$k_2 \simeq$ 1:1:0.01 and 1:0.06:0 for isotactic and syndiotactic PMMA, respectively), distribution of keto-2-picolinyl and ketoquinaldinyl B units is expected to depend on the PMMA precursor stereoregularity: (i) for isotactic copolymers ($k_0 \simeq k_1$), it may be considered nearly Bernouillan, especially for low or moderate $\overline{DS}_m$ ($\overline{DS}_m < 0.5$); (ii) for syndiotactic copolymers where neighboring group effects are stronger ($k_0 > k_1 \gg k_2 \simeq 0$), B units tend to accumulate essentially as isolated units (ABA triads) and as BB diads but to a lesser extent. BBB triads should remain of negligible importance, especially for low $\overline{DS}_m$ ($\overline{DS}_m < 0.3$). For RO and RS copolymers, all the B units should be in the form of isolated units (ABA), assuming in a first approximation $k_1 \simeq k_2 \simeq 0$.

On the other hand, autoretarded kinetics are also an important factor for the narrowing of compositional distribution.[23] The low mean square standard deviation we measured for RO-2 copolymer ($\overline{DS}_m = 0.300$), $\bar{\sigma}^2 = 5.6 \times 10^{-4}$, is fairly similar to that previously noticed for a PMMA functionalized in the same way[2] ($(CH_3)_2NSO_2CH_2Li$/PMMA, $\overline{DS}_m = 0.366$, $\bar{\sigma}^2 = 2.2 \times 10^{-4}$). By comparison, "cross" fractionation of a radically prepared azeotropic styrene–MMA copolymer yields a $\bar{\sigma}^2$ value of 1.6×10^{-4}.[24] According to Frensdorff et al.,[25] a limiting overestimated value of $\bar{\sigma}^2$ may be calculated with the simplifying assumption of the lack of any neighboring group effect ($k_0 = k_1 = k_2$): $\bar{\sigma}^2$ (RO-2) = $\overline{DP}_n^{-1}$ ($\overline{DS}_m - \overline{DS}_m^2$) = 2.3×10^{-4}. The calculated and experimental $\bar{\sigma}^2$ values are not incompatible: besides the limited experimental accuracy, possible local inhomogeneities of the reaction medium arising from inefficient mixing of the reagents with respect to a very fast reaction may contribute to enhance compositional fluctuations in the copolymer.

Alternative Synthesis of the Functionalized PMMA. The only minor disadvantage of the selected substitution process is that it actually requires two moles of the heterocyclic organolithium reagent (reacting first as a nucleophile and then as a base[1]) per ester function. Wolfe et al.[26] proposed a more economical direct acylation of methylated heterocycles in presence of excess sodium hydride according to the following theoretical stoichiometry:



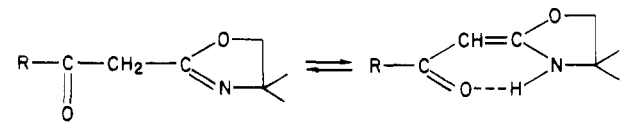
Unfortunately this condensation occurs at a higher temperature (reflux of dimethoxyethane at about 85 °C) where side reactions such as cyclization in B^-B^- diads and chain degradation cannot be completely avoided.[1] More recently[27] the same author, using tertiary carboxamides instead of esters as acylating species, observed significantly improved yields with respect to the organolithium reagent: 70% vs. 50% for the ester. In spite of their lower availability, poly(*N*,*N*-dialkylmethacrylamides) may be of interest for broadening the field of possible polymeric precursors with different solubility properties.

Table IX
Apparent Molar Absorptivities of the Enamine Tautomer for Keto-β-oxazolyl Model and Copolymers in Dilute Solution at 25 °C

		ϵ_{app}, L mol^{-1} cm^{-1}		
		acetonitrile	trifluoroethanol	
sample	$\overline{DS}_m$	λ 282 nm	λ 287 nm	λ 382 nm
model 3	1	20700	11100	0
RO-1	0.133	17500	17600	0
RO-3	0.360	19500	18300	900
RO-4	0.428	18100	19500	1050
RO-5	0.482	17000	14900	1150

Tautomerism on Copolymers. Tautomerism on copolymers involves numerous factors and is indeed a very complex phenomenon: for fixed temperature, solvent, and solution concentration one may theoretically expect as many as 10 different tautomerism constants if the prototropic equilibrium is sufficiently sensitive to compositional and configurational effects in the various B-centered triads (short-range interactions only). The following discussion is restricted to the more salient features of the tautomerism of copolymers with respect to that of their models, except for keto-2-thiazolyl structures where reliable literature data on low molecular weight compounds are still lacking.[5,6] The samples were previously methylated with CH_2N_2[17] whenever necessary to preclude any influence of the few carboxylic acid units on the equilibrium.

Keto-β-oxazolines.



In bulk (25 °C) the model compound and all the RO copolymers show exclusively the chelated enamine structure. Their IR spectra are characterized by the strong specific absorptions of the conjugated enamine structure at 1625 cm^{-1} ($\nu_{C=O}$) and 1530 cm^{-1} ($\nu_{C=C}$) and the lack of any significant absorption bands at 1710 cm^{-1} ($\nu_{C=O}$) and 1670 cm^{-1} ($\nu_{C=N}$ of the oxazoline ring).

For semidilute solution in chloroform, acetonitrile, or dimethylsulfoxide ([B] = 0.15–0.30 mol L^{-1}), ^{1}H NMR measurements at room temperature show that the enamine form is by far the major one for the model (molar fraction > 0.9) and practically the only visible tautomer for sample RO-3 ($\overline{DS}_m = 0.360$). A temperature increase to 80 °C barely shifts the equilibrium toward the ketonic form, which amounts to a molar fraction of about 0.12 and less than 0.10 for the model and RO-3 copolymer, respectively. It does appear with significant weight for the model in trifluoroethanol (molar fraction of about 0.40), and it is finally the only stable tautomer for all the samples in strongly acidic media such as trifluoroacetic acid (protonated form). In dilute solution in acetonitrile and trifluoroethanol where Beer's law is well obeyed (25 °C, 0.3 < [B] × 10^3 mol L^{-1} < 1.5) the model and the copolymers show a single strong absorption within the range 282–290 nm. Addition of trifluoroacetic acid induces its progressive

Table X
Enol and Enamine Fraction F for Keto-2-picolinyl and Ketoquinaldinyl Models and Copolymers in Dilute Me_2SO Solution (0.6%) at 25 °C

keto-2-picolines			ketoquinaldines		
sample	$\overline{DS}_m$	F(enol)	sample	$\overline{DS}_m$	F(enamine)
model 1	1	0.24	model 2	1	0.72
model 1	1	0.21[a]	model 2	1	0.69[a]
IP-0	0.040	0.54	IQ-0	0.049	0.88
SP-0	0.017	0.52	SQ-0	0.026	0.94
RP-1	0.123	0.52			
RP-2	0.313	0.59			
IP-2	0.311	0.65	IQ-1	0.321	0.88
IP-2	0.311	0.45[a]	IQ-1	0.321	0.81[a]
SP-2	0.298	0.67	SQ-1	0.223	0.97
SP-2	0.298	0.60[a]	SQ-1	0.223	0.88[a]
RP-3	0.538	0.62			
RP-4	0.615	0.66			

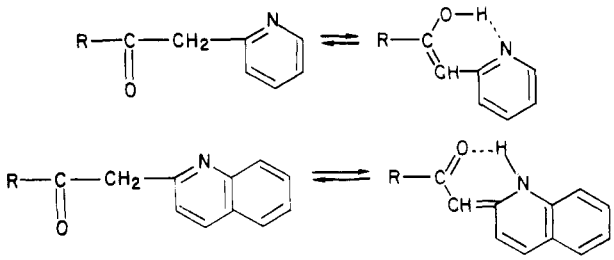
[a] Value at 70 °C.

decrease and the simultaneous increase of a band at λ 270 nm, characteristic of the protonated ketonic form. The higher wavelength absorption mainly arises from the π–π^* transition of the conjugated enamine structure. Under the assumption that its molar absorptivity is independent of chain structure, the comparison of the *apparent* molar absorptivities of the various samples (calculated with respect to the total B unit content) given in Table IX suggests the following comments: (i) With neglect of the RO-5/TFE system, ϵ_{app} is nearly constant, of about 18 200 ± 1300 L mol^{-1} cm^{-1} for all the other copolymer solutions; the prototropic equilibrium is thus probably independent on chain composition. Such a behavior may arise from the fact that all the tautomerizable B units are isolated in AB̆A triads for all the RO copolymers (see previous section).

(ii) The chelated enamine structure is always the major one (molar fraction > 0.8) for copolymers, whatever the solvent is. For the model, however, the enamine fraction is drastically decreased by a factor of about 2 when going from acetonitrile to trifluoroethanol.

(iii) We have no satisfactory explanation for the long-wavelength absorption at λ 382 nm that is observed in trifluoroethanol solution only for sufficiently substituted copolymers ($\overline{DS}_m$ > 0.20).

Keto-2-picolinyl and Ketoquinaldinyl Structures.[13-16,27]



Representative data on the keto–enol and keto–enamine equilibria for RP and RQ copolymers studied by ^{1}H NMR spectroscopy in dilute solution in Me_2SO at 25 °C (0.6 g dL^{-1}) are given in Table X. Some important features may be outlined:

(i) The low steady increase of the enol fraction with $\overline{DS}_m$ observed for predominantly syndiotactic copolymers may be tentatively correlated with the simultaneous increase of ABB triads (see previous section).

(ii) Comparison of iso- and syndiotactic samples of very low $\overline{DS}_m$ ($\overline{DS}_m$ < 0.05), where nearly all the B units are isolated in A_mB_mA or A_rB_rA triads, respectively, shows that stereoregularity effects are quite negligible.

(iii) A temperature increase to 70 °C shifts the equilibrium toward the ketonic form by disrupting the chelating hydrogen bond, which is the major factor stabilizing the conjugated tautomer.[7]

(iv) For all copolymers the chelated conjugated form is highly favored with respect to the model compounds. The ketonic tautomer is nearly negligible (molar fraction of about 0.1) in the case of the ketoquinaldinyl copolymers, as in the previous case of keto-2-oxazolyl samples. Solvent effects in semidilute solution (6 g dL^{-1}) in aprotic solvents at 25 °C were compared for the model and the RP-2 sample ($\overline{DS}_m$ = 0.313) (Table XI). An increase of the solvent polarity, expressed in terms of the Dimroth–Reichardt E_T polarity parameter,[28] shifts the equilibrium toward the more polar ketonic tautomer, in good agreement with literature data;[13,15] these effects, however, are significantly reduced for the copolymer with respect to the model compound. In strongly acidic solvents, only the protonated ketonic tautomer is actually stable.[13]

When short-range interactions around the tautomerizable B unit are considered, the two most specific features of the tautomerism on copolymers may be readily explained on the basis of the well-known behavior of their low molecular weight models.

Since chelation induces an "ordered" and "planarized" structure,[15] the enol and enamine forms show decreased polarity and bulkiness with respect to the ketonic one; in copolymers, where steric hindrance and polarity are respectively enhanced and lowered by the backbone and the lateral groups, the chelated conjugated structure is highly favored. For comparison, it has been reported that the modifications of local steric hindrance and conformation involved by enolization respectively increase and decrease the extent of enolization for poly(methacryloylacetone) and for poly(vinyl acetoacetate) or linear macromolecular keto-β-esters.[8,9]

Moreover a fraction of the solvation sphere around the B site is excluded to the solvent by the neighboring groups of the polymeric chain of constant polarity: solvent effects are thus significantly reduced with respect to those observed for the model compound. For comparison, the tautomerism of poly(vinyl acetoacetate) is nearly insensitive to solvent polarity.[8]

Conclusion

The nucleophilic substitution of 2-picolinyl- and quinaldinyllithium (20 °C) and of [(4,4-dimethyl-2-oxazol-2-yl)methyl]lithium (−15 °C) onto PMMA in aprotic solution affords a versatile and general synthetic pathway toward homogeneous binary copolymers functionalized with keto-β-heterocyclic structures. The reaction is quite selective, and all the important structural parameters of the

Table XI
Enol Fraction F for Keto-2-picolinyl Model and Copolymer RP-2 ($\overline{DS}_m$ = 0.313) in Semidilute Solution in Various Solvents at 25 °C

solvent E_T, kcal mol^{-1}	C_6H_6 34.5	C_5H_5N 40.2	$ClCH_2$–CH_2Cl 41.9	CH_3COCH_3 42.2	CH_3SOCH_3 45.0	CF_3CO_2H
F(model 1)	0.410	0.315	0.270	0.250	0.215	0
F(RP-2)	0.580	0.510	0.490	0.510	0.450	0

copolymers, such as composition, $\overline{DP}_n$, and tacticity, may be easily controlled. The keto–enol or keto–enamine prototropic equilibria of the new functional groups are preserved in the copolymers with specific features arising from the characteristic short-range interactions within the solvation sphere of the tautomerizable lateral group. As a special point of great interest, tautomerism may be considered as a potential probe to test the local polarity of the microenvironment of macromolecules in solution: this new approach, which we have briefly reported elsewhere,[29] will be comprehensively discussed in a forthcoming publication.

Experimental Section

Uncorrected melting points were taken on a Mettler FP 5 capillary melting point apparatus. IR, UV, and ^1H NMR spectra (chemical shifts δ expressed in ppm, downfield from Me_4Si used as internal reference) were obtained respectively on a Perkin-Elmer 237, Beckman Acta V, and Perkin-Elmer R-24 (60 MHz) or Cameca 250 (250 MHz) spectrometer. Since the tautomerism equilibrium is not reached instantaneously after the dissolving process, the measurements were systematically and safely performed after at least 15 h annealing of the solutions at room temperature and 1 h annealing at the selected measurement temperature.

Potentiometric measurements were carried out under argon on a Metrohm E-436 potentiometer fitted with various electrodes: glass–calomel EA-121 for the $(CH_3)_3COK$/THF and ClO_4H/CH_3CO_2H systems and glass–calomel–DMF (Tacussel DMF-B) for the CH_3ONa/DMF system.

Specific index increments were measured at 25 °C on a Brice-Phoenix BP 1000 V differential refractometer for λ 5460 Å. Light scattering measurements were performed on a Fica apparatus at room temperature for the same wavelength. Osmometry measurements were carried out on a Mechrolab-52 apparatus fitted with SS-08 membranes from Schleicher and Schuell, using dioxane solution at 30 °C. Fractionation was carried out at 20 ± 0.1 °C in a standard way by successive precipitation, adding increments of nonsolvent into the copolymer solution (1.5% w/v as initial concentration).

Solvents, Reagents, and Polymers. After convenient purification and drying (see below), solvents were directly distilled and stored under argon in Schlenk vessels: THF and benzene were distilled from disodiumbenzophenone dianion, HMPA from the Na–HMPA complex, Me_2SO, DMF, tetramethylethylenediamine (TMEDA), and methylpivalate from CaH_2. 2-Picoline, quinaldine, 2,4,4-trimethyl-2-oxazoline, 2-methyl-2-thiazoline, pivalonitrile, and pivaloyl chloride were vacuum distilled on a Cadiot teflon spinning-band column. Ether solutions of diazomethane were prepared and titrated according to literature.[30] Potassium *tert*-butoxide was purified by sublimation,[19] and its THF solutions were stored under argon. For UV and NMR measurements solvents of "spectrophotometric grade" were systematically dried over molecular sieves 4A.

Polymers. Isotactic[31] and syndiotactic[32] PMMA (purity in triads of more than 97%) were prepared according to literature procedures; in order to reduce polydispersity, the fractions of the highest and the lowest molecular weights were removed by preferential extraction using respectively the two following solvent–nonsolvent systems: C_6H_6–CH_3OH 1:1 (v/v) and $CHCl_3$–n-C_6H_{14} 1:3 (v/v) PMMA-I: $\bar{M}_w = 2.35 \times 10^5$, $\bar{M}_n = 5.76 \times 10^4$; After fractionation: PMMA-S: $\bar{M}_w = 2.31 \times 10^5$, $\bar{M}_n = 1.06 \times 10^5$. The radical PMMA sample from Rohm and Haas ($\bar{M}_w = 9.5 \times 10^4$, $\bar{M}_n = 6.5 \times 10^4$) has a predominantly syndiotactic structure: % I = 5, % H = 37, % S = 58.

Organolithium Compounds. Experiments involving lithium and organolithium reagents were carried out under a slight pressure of argon in an all-Pyrex glass reactor allowing the use of vacuum and argon sweeping cycles. Solvents and reagents were introduced under argon from Schlenk vessels or through self-sealing rubber caps by using a syringe technique. Solutions of n-butyllithium in benzene (0.5–1.5 N) were titrated in Me_2SO against acetanilide in the presence of triphenylmethane as a color index.[33] Phenyllithium and all the $HetCH_2Li$ solutions were prepared through metallation of the precursor hydrocarbon by stoichiometric amounts of n-BuLi according to literature procedures: C_6H_6/n-BuLi in presence of TMEDA/20 °C;[34] 2-picoline/n-BuLi/THF/−30 °C;[35] quinaldine/C_6H_5Li/C_6H_6/20 °C;[4] 2,4,4-trimethyl-2-oxazoline/n-BuLi/THF/−70 °C;[5] 2-methyl-2-thiazoline/n-BuLi/THF/−70 °C.[6]

Synthesis of Model Compounds. Acidity and basicity equivalents refer to titration by $(CH_3)_3COK$ and $HClO_4$, respectively (see Results).

***tert*-Butyl 2-Picolinyl Ketone (Model 1).** To a solution of 0.30 mol of 2-picolinyllithium is added dropwise 20 mL (0.15 mol) of methyl pivalate, the temperature being kept below 35 °C. After 1 h of stirring, the reaction is quenched by 0.30 mol of CH_3CO_2H, and the solvent is removed on a rotary evaporator. The residue dispersed in H_2O is extracted with Et_2O, and the organic phase is dried over anhydrous Na_2SO_4 and concentrated to a crude oil, which affords by vacuum distillation 23.2 g of (1) (87.1% yield) as a dark red liquid. Acidity equivalent 1.00; basicity equivalent 1.01. NMR (CF_3CO_2H solution, ketonic form) δ 0.93 (s, 9 H, $(CH_3)_3$), 4.10 (s, 2 H, $COCH_2Het$), 7–8.5 (m, 4 H, pyridine nucleus). Anal. Calcd for $C_{11}H_{15}ON$: C, 74.54; H, 8.53; O, 9.03; N, 7.90. Found: C, 74.30; H, 8.58; O, 9.18; N, 8.03.

***tert*-Butyl Quinaldyl Ketone (Model 2).** To a solution of 0.1 mol of quinaldyllithium is added dropwise 8.31 g (0.1 mol) of pivalonitrile, the temperature being kept below 35 °C. After being stirred for 24 h, the solvent is removed on a rotary evaporator, and the residue is dispersed in dilute SO_4H_2 at a temperature not greater than 30 °C. After being stirred at room temperature for 12 h, pH being kept acidic, the medium is extracted with Et_2O and the organic phase dried over anhydrous Na_2SO_4. Removal of the solvent to dryness affords the crude model 4; precipitation of its CH_3OH solution into H_2O yields 21.1 g of pure orange crystals (93% yield): mp 65.0 °C; acidity equivalent 1.04; basicity equivalent 1.00; NMR (CF_3CO_2H, ketonic form) δ 0.95 (s, 9 H, $(CH_3)_3$), 4.25 (s, 2 H, $COCH_2Het$), 7.20–8.70 (m, 6 H, quinoline nucleus). Anal. Calcd for $C_{15}H_{17}ON$: C, 79.26; H, 7.54; O, 7.04; N, 6.16. Found: C, 79.19; H, 7.43; O, 7.16; N, 6.27.

Models 3 and 4. To a solution of 0.15 mol of the corresponding $HetCH_2Li$ at −70 °C is added dropwise 6.03 g (0.05 mol) of pivaloyl chloride diluted in 4 volumes of THF, and stirring is maintained during 3 h at −70 °C. Temperature is then progressively raised to −10 °C, and the reaction is quenched by 0.15 mol of CH_3CO_2H. CH_3CO_2Li is eliminated by filtration or centrifugation, and the resulting clear solution is evaporated to dryness on a rotary evaporator. The residue is diluted into $CHCl_3$, the organic phase is washed with H_2O, dried over anhydrous Na_2SO_4, and evaporated to dryness, affording crude models 3 and 4.

***tert*-Butyl 2,4,4-Trimethyl-2-oxazolyl Ketone (Model 3).** Recrystallization in heptane yields 5.9 g of white crystals (60% yield): mp 93.2 °C; acidity equivalent 0.98; basicity equivalent 1.00; NMR ($CDCl_3$, more than 90% of enamine form) δ 1.14 (s, 9 H, $(CH_3)_3$), 1.39 (s, 6 H, $(CH_3)_2$), 4.07 (s, 2 H, $OCH_2C(CH_3)_2$), 5.05 (s, 1 H, COCH=Het), 9.68 (1 H, NH). The ketonic form shows very weak resonance peaks at δ 1.18 (s, $(CH_3)_3$), 1.30 (s, $CH_3)_2$), 3.49 (s, $COCH_2Het$), 3.94 (s, $OCH_2C(CH_3)_2$). Anal. Calcd for $C_{11}H_{19}O_2N$: C, 66.97; H, 9.71; O, 16.22; N, 7.10. Found: C, 67.02; H, 9.66; O, 16.24; N, 7.06.

***tert*-Butyl 2-Methyl-2-thiazolyl Ketone (Model 4).** Evaporation of the $CHCl_3$ solution affords 3.6 g of pale yellow crystals (39% yield): mp 112.0 °C; NMR ($CDCl_3$, enamine form) δ 1.05 (s, 9 H, $(CH_3)_3$), 3.05 (t, 2 H, CH_2), 3.70 (t, 2 H, CH_2), 5.35 (s, 1 H, COCH=Het). Anal. Calcd for $C_9H_{15}ONS$: C, 58.34; H, 8.16; O, 8.63; N, 7.56; S, 17.31. Found: C, 58.43; H, 8.36; O, 8.73; N, 7.77; S, 17.28.

Dimerization of (Benzoxazol-2-yl)methyllithium. In the same experimental conditions as for models 3 and 4, the reaction does not lead to the expected *tert*-butyl 2-methylbenzoxazolyl ketone. Recrystallization of the crude reaction product in hexane affords yellow crystals (65% yield with respect to the dimerization process) of a dimer showing two tautomers in equilibrium (see Discussion): mp 133.5 °C. Anal. Calcd for $C_{16}H_{14}O_2N_2$: C, 72.16; H, 5.30; O, 12.02; N, 10.52. Found: C, 71.63; H, 5.41; O, 12.70; N, 10.15.

General Procedure for the Chemical Reactions onto PMMA. The PMMA solution in THF + HMPA (precooled to the desired temperature if necessary) is rapidly added under

efficient stirring into the organolithium solution (THF + C_6H_6) kept at the selected temperature. In most cases, concentrations are within the following ranges: [PMMA] = 0.2–0.4 mol L^{-1}, THF–C_6H_6–HMPA = 4:3:1 (v/v). The initial ratios $[HetCH_2Li]_0/[PMMA]_0$ and the reaction times and temperatures are given in Tables VII and VIII. At the end of the reaction, the medium is quenched by stoichiometric amounts of CH_3CO_2H ($[CH_3CO_2H]/[HetCH_2Li]$ = 1); after removal of CH_3CO_2Li by filtration or centrifugation, the clear solution is concentrated on a rotary evaporator and precipitated into a large excess of a CH_3OH–Et_2O mixture (1:3 v/v). The isolated copolymer is thoroughly washed overnight under efficient stirring in H_2O–CH_3OH mixtures, filtered, and vacuum dried. The final purification step is carried out by precipitation of the copolymer solution in acetone (DMF for the higher $\overline{DS}_m$) into a large excess of CH_3OH–Et_2O (1:3 v/v).

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Effects of Dibutylmagnesium on Alkyllithium-Initiated Polymerizations

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ABSTRACT: Dialkylmagnesium, by itself, is not an active initiator for diene and styrene polymerization, but it participates in polymerization when complexed either with the alkyllithium initiator or with the propagating polymer–lithium molecules. In the latter case a bimodal distribution is formed. For butadiene the participating factor, which is defined as the ratio of the effective amount of dibutylmagnesium participating in the initiation to the total amount of dibutylmagnesium initially charged, is in the range 1.1–1.4 in cyclohexane and 1.5–1.8 in cyclohexane/THF. For styrene, the participating factor is around 0.7 in cyclohexane and 1.4–1.9 in cyclohexane/THF. A 1:1 complex and an equilibrium between a 1:1 and a 2:1 complex are proposed to explain the observed results. The presence of R_2Mg retards the rate of polymerization, but it does not affect the stereochemistry of the diene polymerization.

Introduction

Alkyllithium can form complexes with other metal alkyls such as those of Mg, Zn, and Cd; e.g.

$$\tfrac{1}{2}(LiR)_4 + MR'_2 \rightarrow Li_2MR_2R'_2$$

Thus, methyllithium was reported to form a 2:1 complex with $(CH_3)_2Mg$ in tetrahydrofuran solution, whereas the proton and lithium-7 NMR spectra of the zinc system are consistent with an approximately equal molar mixture of 2:1 and 1:1 complexes.[1] Only the 1:1 complex predominates in the cadmium system. Lithium and methyl group exchange between the excess methyllithium and the complex in each system occurs at a comparably rapid rate. In diethyl ether solution, however, 2:1 and 3:1 complexes were found for all three metal alkyls, although there has been no evidence obtained for or against the formation of a 1:1 complex with methyllithium.

Smets and his co-workers[2] reported that a 1:1 complex between ethyllithium and diethylzinc was formed in pure benzene. Another example of 1:1 complex formation is

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