2766 *Macromolecules* **2001,** *34,* 2766−2775

A New Polyhydrocarbon−Polyamine AB Block Copolymer

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Received November 14, 2000; Revised Manuscript Received February 13, 2001

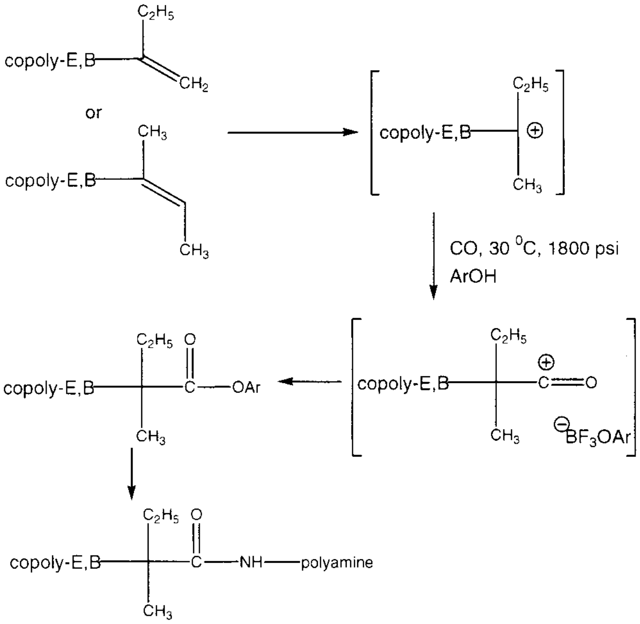
ABSTRACT: Copolymers of ethylene and 1-butene were synthesized using a single-site zirconium-based coordination catalyst. The polymers terminated exclusively in 1-butene ends, predominantly ethylvinylidene. They were carbonylated under Koch−Haaf conditions using boron trifluoride, carbon monoxide, and phenols to give polymeric hydrocarbons containing a single carboaryloxy group. Both 1,3- and 1,5-rearrangements were observed in this synthesis. The amination reaction with polyethylene amines followed second-order kinetics, but with a steadily decreasing bimolecular rate constant. The physical properties along with the block composition of the resulting polyhydrocarbon polyamine make this a potential candidate for motor oil dispersant. To interpret the polymer results, appropriate model compounds consisting of appropriately branched carboxylic acids, aryl esters, and amides were synthesized. The ^{13}C NMR and IR spectra, both of the quaternary carbons and the carbonyls, supported the structure assignment for the polymers. Finally, the kinetics of the reactions of the model esters with model monoamines *N*,*N*-dimethyltrimethylenediamine and *N*-2-(ethylamino)piperidine quantitatively reproduced the amidation kinetics observed for the polymeric ester.

Introduction

The search for new motor oil additives continues with the goal of obtaining higher performance materials. These materials require the coupling of a nonpolar polyhydrocarbon moiety, necessary for oil solubility, with a polar moiety, particularly polyethylene amines, necessary for the chelating of iron and other metal particles. It has been a great synthesis challenge to devise efficient methods to couple such disparate parts. Conventionally, these additives have been formed by the ene reaction of maleic anhydride with polyisobutylene, resulting in an electrophilic succinic anhydride derivative, which can then be reacted with polyethylene amines.[1] In this paper, we describe a new synthetic route in which a hydrocarbon polymer derivatized with an electrophilic terminal aryl ester group is coupled to a polyethyleneamine.

Our concept (Scheme 1) involves converting the terminal double bond of a copolyolefin to an acyl functionality using a Lewis acid and carbon monoxide. A polymer tertiary carboxyl function would be achieved by this reaction, which is reacted directly with a suitable phenol. Finally, amidation would be carried out with polyethyleneamine.

Scheme 1. Synthesis of the Polyhydrocarbon with Terminal Aryl Ester



The area of single-site coordination polymerization of olefins has undergone enormous growth since the pioneering discovery of Kaminsky.[2] Various transition metals complexed to suitable ligands have been employed, resulting in increased control of the polymerization process (single-site catalysis reviews[3,4]). We chose a dimethylsilylene-bridged zirconium catalyst activated with methylalumoxane for the copolymerization of ethylene and butene.[5−9]

The carbonylation of the hydrocarbon polymer is patterned after the original discovery of Koch and Haaf,[10,11] who used anhydrous formic acid as both the acid and CO source. Although carboxylic acids are the usual products of such carbonylations, it can also be run in the presence of a phenol, leading immediately to an aryl ester. The intermediate carbenium ion can isomerize to give neo acid structures suitable for our purpose. A wide variety of other Bronsted and Lewis acids has been used for the Koch−Haaf reaction; BF_3 in particular has been utilized extensively by Soviet investigators.[12−16]

The linking of the polyamine with the polyhydrocarbon polymer will be accomplished by ester aminolysis, which is a well-known reaction. It is especially facile with phenyl esters in which the ring carries an electron-attracting group. Many kinetics studies have been reported inasmuch as the reaction is usually quantita-

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10.1021/ma001947o CCC: $20.00

Table 1. Coordination Copolymerization Conditions and Properties of the Resulting EB Copolymers[2,a]

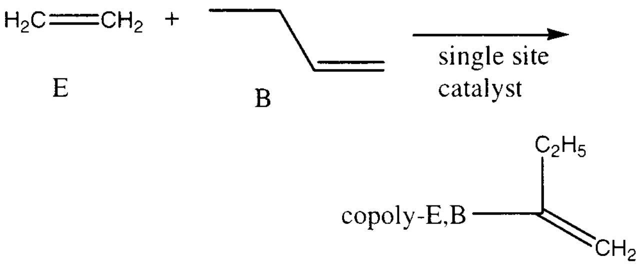
polymer	feed, % ethylene[b]	temp (°C)[c]	press. (bar)[c]	residence time (min)[c]	M_n[d]	MWD[d]	wt % E[e]	S_f[f]	ESL[g]	pour point[h] (°C)	ethylvinylidene terminals[i] (%)	vinyl terminals[j] (%)
1	8.5	71	13	60	4666	2.3	22.8	0	1.55	−30	69.6	0
2	19	80	16.5		4325	2.34	39	0	2.16	−36	66.3	0
3	12.9	90	19	30	2797	2.15	17	0	1.54	−30	63	0
4	27	96	23		8027	2.74	55	0.6	3.24	−18	50.3	4.8
5	22	125	1330	1	2000	3.6	55	9	2.84	−33	68	

[a] The details of the data presented in this table and the procedures are described in the Experimental Section and in ref 2. [b] Ethylene gas added to a liquid stream of 40 wt % 1-butene and 60 wt %% isobutane. [c] Reactor conditions for polymerization. [d] Number-average molecular weight and molecular weight distribution determined by GPC. [e] Weight % ethylene in the final copolymer as determined by ^{1}H NMR. [f] Scattering factor as determined by light scattering. [g] Ethylene sequence length as determined by ^{13}C NMR. [h] Pour point as determined according to ASTM method no. D97. [i] End group determination by ^{1}H NMR.

tive. (see below) This reaction at a tertiary carboxylic function might be slow. However, an extremely stable, sterically hindered amide bond would join the polyhydrocarbon and polyamine blocks.

Results and Discussion

Coordination Copolymerization of Ethylene and 1-Butene.[17] The hydrocarbon polymers were synthesized using ethylene (E) and 1-butene (B) by coordination polymerization using a single site catalyst. A representative catalyst used consisted of 1,1-dimethylsilylene bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride in the presence of methylalumoxane, with a ratio of Al:Zr of 500:1. Termination occurred almost exclusively from 1-butene ends, so that most polymer chains have a terminal ethylvinylidene group.



As shown in Table 1, these polymers can be formed with varying ethylene content and molecular weight depending on the reaction conditions and ethylene feed. The ethylene content was determined by proton NMR, as was the nature of the terminal group. Roughly 60% of the chains were found to have a terminal ethylvinylidene unsaturation. The molecular weights and MWD were determined by gel permeation chromatography.

Light scattering was used to determine the degree of aggregation, S_f. For use as motor oil viscosity modifiers, this should be zero, i.e., an absence of aggregation. Polymers 1−3 in Table 1 fulfill this requirement. The pour points, which are uniformly around −30 °C, are appropriate for motor oil use. ^{13}C NMR was used to obtain the average ethylene sequence length, ESL. A small number for ESL corresponds to insufficient ethylenic crystallinity to act as crystallization sites for copolymer aggregation or to participate in the crystalline wax network formed as the mineral oil solvent is cooled. We sought EB copolymers with sufficient ethylenic crystallinity to aggregate after quenching, but which is insufficient to contribute to the wax crystalline network. An ethylene content of 20%−40% and molecular weight of 2700−4700 gave the best results. All these data are summarized in Table 1.

Koch−Haaf Functionalization to Polymer Aryl Esters.[18] These vinyl-terminated polymers are derivatized in a Koch−Haaf reaction, in which the vinyl group of the polymer is protonated with a strong acid to form a carbocation, which traps the carbon monoxide and an alcohol present in the reaction vessel to produce an ester (polymer−COOR). In the reactions in this study, phenols were used as the alcohol, for reasons explained below. Extensive studies on the Koch−Haaf carbonylation led to the conclusion that boron trifluoride was the preferred catalyst.[12−16]

As mentioned, ethylene−butene (EB) copolymers produced with metallocene catalysts terminate almost exclusively with a butene monomer to yield an ethyl-substituted vinylidene double bond; a small portion of the corresponding trisubstituted olefin isomer is also anticipated (Scheme 1). Protonation of these terminal olefins yields the same methyl, ethyl, and polymer-substituted tertiary carbocation. Trapping the carbocation in a Koch reaction with carbon monoxide and a phenol leads to virtually 100% neosubstituted polymeric phenyl ester, with either ethylene E or butene B as the penultimate monomer. The EB end group is less sterically hindered than the BB end group, which contains an additional branch in the γ-position. Thus, the carbonylation of the terminal vinylidene group is expected to produce at least two distinct ester environments with potentially different reactivities.

The Koch−Haaf reaction was carried out in the presence of suitable phenols, which were chosen because phenyl esters will be reactive in the desired amidation reaction with polyethylene amines. Careful attention had to be paid to the nature of the phenol. Electron-attracting substituents on the phenol were preferred for two reasons. First, these substituents prevented Friedel−Crafts alkylation by the carbenium ion, as opposed to the desired O-acylation by the acylium ion. Second, they gave better leaving groups in the subsequent reactions. An incidental important side benefit of utilizing these electron-poor phenols lay in the ready recovery of the boron trifluoride catalyst by distillation from the reaction mixture, because the electrophilic substituents weaken the BF_3 complexation. In the best example an ethylene/1-butene copolymer of M_n 4600 was treated with BF_3 gas in the presence of CO and 2,4-dichlorophenol, which led to 85% yield of the desired ester-terminated polymer. Other halogenated phenols, such as *p*-chloro-, *o*-chloro-*p*-methyl-, or *m*-fluorophenol, also gave satisfactory results.

Polymer Aryl Ester Reactions. Any amine with a primary NH_2 moiety is capable of reacting with the ester group of the functionalized hydrocarbon polymer. The preferred amines for use as dispersants in motor oil applications are polyethyleneamines with an average

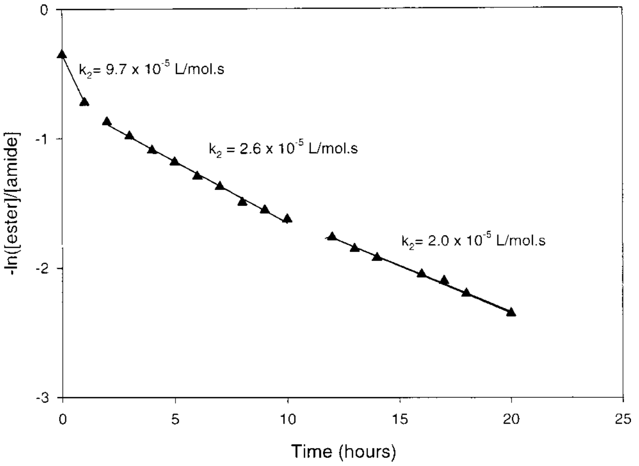


Figure 1. Second-order plot for the aminolysis of a polyhydrocarbon 2,4-dichlorophenyl ester at 200 °C as followed by FTIR.

molecular weight greater than 230, because they have little or no volatility under the reaction conditions. Aminolysis of the EB copolymer 2,4-dichlorophenyl ester with polyethyleneamine at 180 °C proceeded to a conversion of 65% in 7 h. This conversion jumped to 98% when the reaction was run at 0.05 Torr for 7 h, as determined by ^{13}C NMR and IR spectroscopy.[19]

The degree of conversion is monitored by tracking the disappearance of the ester absorption band in the carbonyl region of the infrared spectrum. Significant deviations from simple second-order kinetics are observed. Figure 1 shows the conversion to amide of the EB copolymer (i.e., decrease of the ester carbonyl absorption in the IR spectrum). As the reaction proceeds, the rate slows dramatically, with the initial constant up to 10−40-fold faster than the final rate constant in some cases, depending on the nature of the phenol and reaction temperatures.

The slowing of the reaction is attributed to the presence of ester structures with differing reactivities due to varying extent of steric hindrance at the positions adjacent to the carbonyl group. At the beginning of the reaction, the less hindered components react rapidly, giving an apparent high rate constant. As these components are depleted, the more hindered esters predominate and the reaction slows, causing deviations in the second-order rate behavior.

Moreover, ^{13}C NMR spectral investigations of these polymeric esters revealed clear differences in the carbonyl and quaternary carbon regions, an indication of two distinct environments: one set of peaks at 46−47 ppm, depending on the phenol, and the other peaks at 49−50 ppm (Figure 2). A correlation was found between the deviations from second-order kinetics and the relative ratios of these peaks in the ^{13}C NMR spectra with more reactive polymers containing more of the high field absorptions. Figure 3 shows the distribution of the more hindered and less hindered ester functionalities as the amination reaction progresses, as monitored by FTIR. The less hindered esters, i.e., the ones with the higher field signals in the ^{13}C NMR spectra react faster.

These deviations from expected second-order behavior are much greater than could be attributed to the effect of penultimate monomer unit. This prompted us to look more closely at the polymer aryl ester structure. As mentioned above, we assume that the hydrocarbon polymer chains all end in a butene unit, and then two chain ends are possible depending on the penultimate unit, namely a BB (butene−butene) or an EB (ethylene−butene) end. The ^{13}C NMR spectra of the quaternary and carbonyl carbons of the polymer (Figure 2) show that the polymeric phenyl esters exist in more than the two forms originating from the two penultimate monomers. We thought it highly unlikely that the ante-penultimate unit would exert an influence on the reaction rate. So the polymer had to contain rearranged structures.

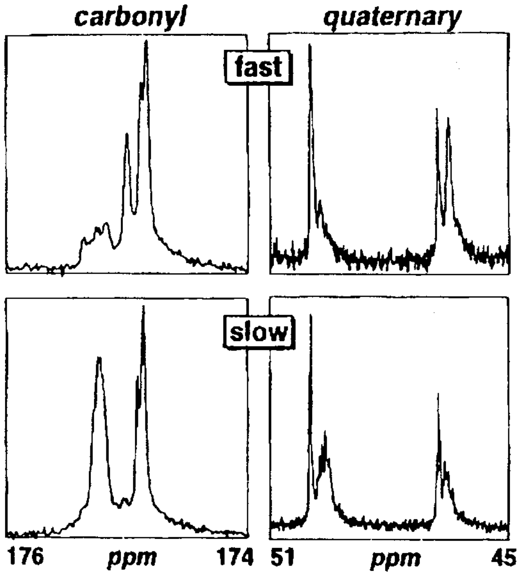


Figure 2. ^{13}C NMR spectra of the carbonyl carbon and the quaternary carbon of a polyhydrocarbon 2,4-dichlorophenyl ester.

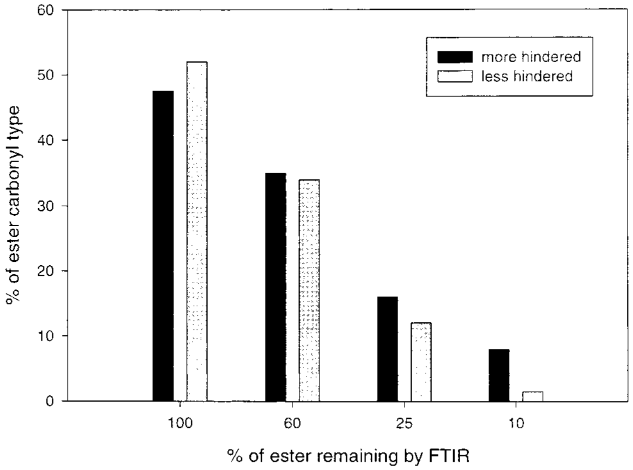
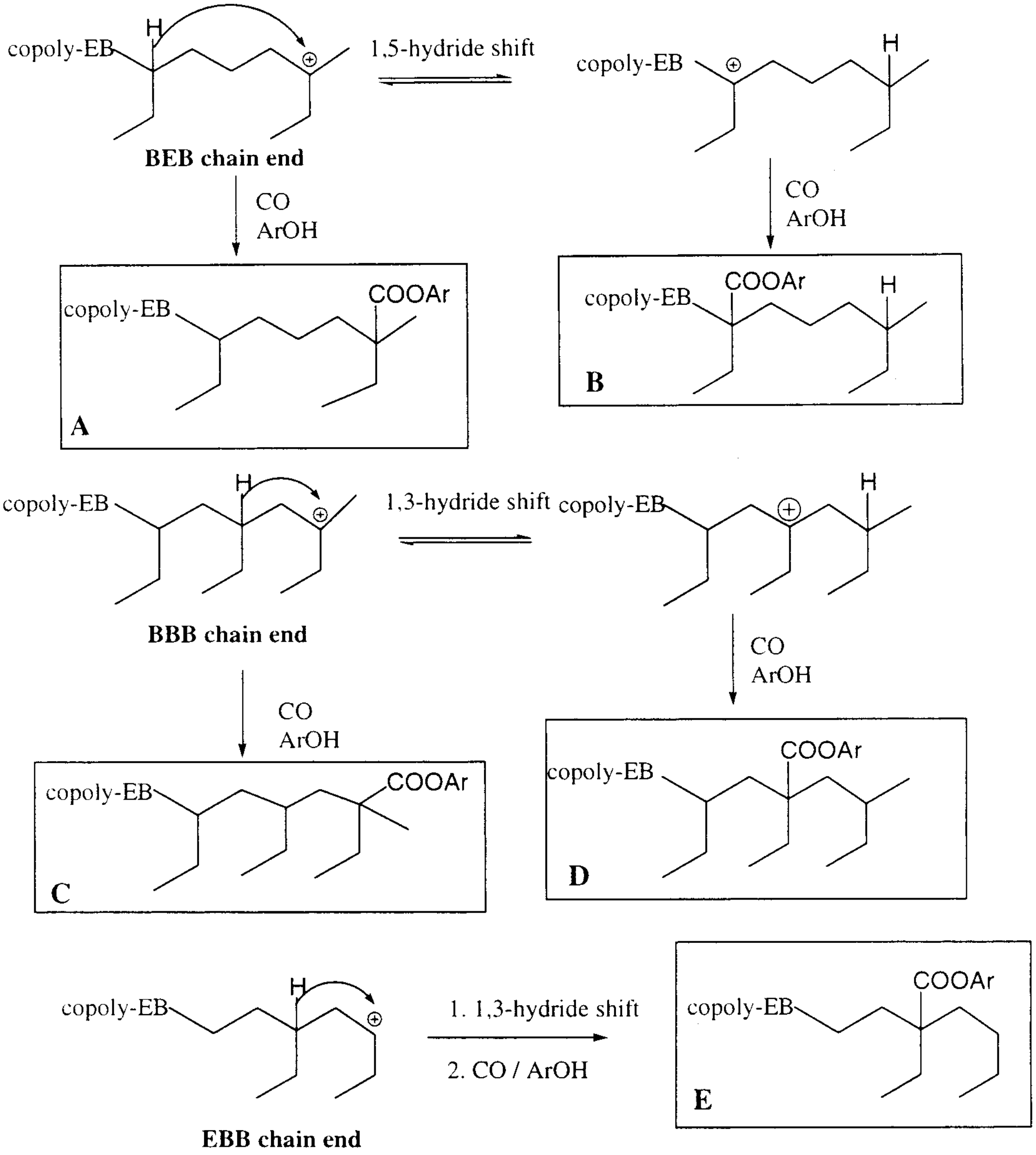


Figure 3. Comparison of the disappearance rates of the carbonyl carbons of varying reactivities in ^{13}C NMR.

As shown in Scheme 2, we can envision several pathways during the Koch−Haaf reaction based on the terminal units in the hydrocarbon polymer. 1,2-Hydride shifts to convert a tertiary carbocation into a secondary carbocation have a high activation energy and should not be facile at the relatively low temperatures and in the low-polarity medium employed for the Koch−Haaf reaction. Indeed, ^{13}C NMR spectra confirm the absence of any carbonyl groups attached to a secondary carbon. A reasonable interpretation for the additional phenyl ester isomers was found in the occurrence of 1,3- and 1,5-hydride shifts in the protonated polymer. We propose that there are three possible chain end structures which would be susceptible to these hydride shifts,

Scheme 2. End Groups Expected with Hydride Shift in the Koch–Haaf Reaction



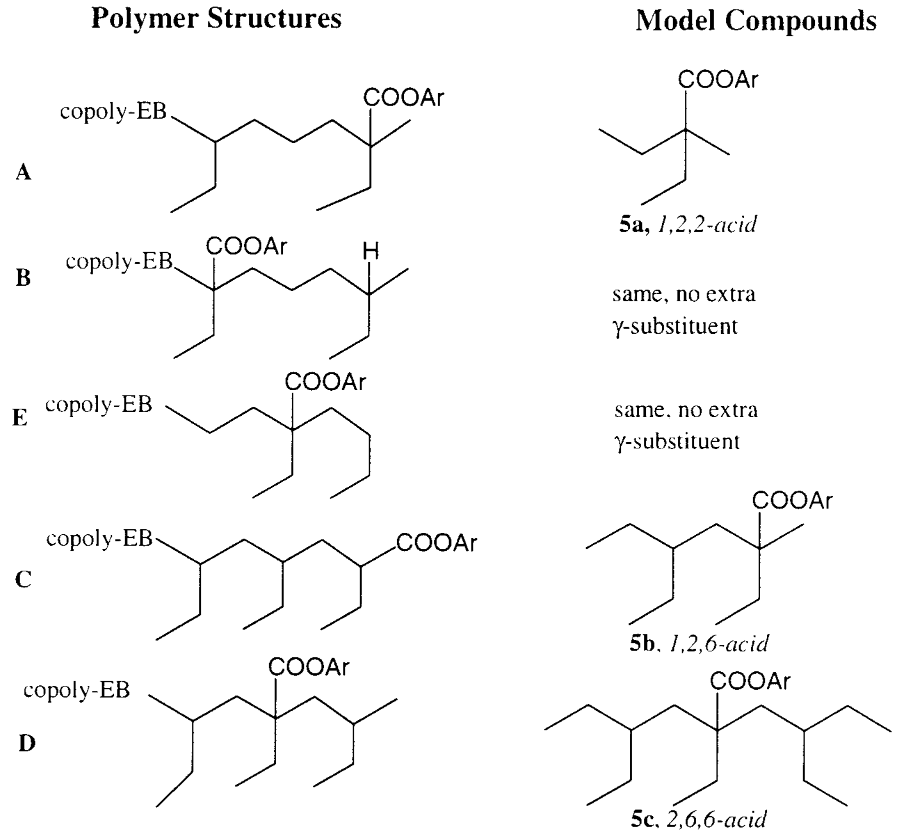
namely a BEB chain end or BBB and EBB chain ends. We also know that the activation energy for rearrangement (6–8 kcal/mol) is lower than the activation energy for the carbonylation (~11 kcal/mol).[20] The proposed rearrangements in Scheme 2 lead to more hindered esters. The fourth possibility is a 1,4-rearrangement, which is thermally forbidden according to orbital symmetry rules. Thus, in our view, five distinct structural environments are likely to be produced during the carbonylation process, namely two unrearranged products **A** and **C**, and three rearranged products, **B**, **D**, and **E**, which differ in the extent of branching in the γ-position, as shown in Scheme 2.

The unrearranged aryl esters are terminal and therefore less sterically hindered than the rearranged ones. We therefore made the assumption that the fast amination reactions corresponded to the former. This assumption was verified by the comparison of the polymer ^{13}C NMR signals for both the quaternary and carbonyl carbon, which corresponded to the ^{13}C NMR signals of the appropriate model esters, synthesized and characterized, as described below (Scheme 3).

Synthesis of Model Compounds for Polymer Aryl Esters. Model compounds were synthesized for comparison of the carbonyl groups of the polymers in the spectra and for a detailed kinetics study examining the influence of the substitution pattern at the α-carbon and beyond on the amination rate of neosubstituted phenyl esters.

Model compounds for the polymer aryl esters were selected to mimic the environments for both the unrearranged esters and for two of the rearranged esters, i.e., on the basis of their resemblance to the expected polymer ends (Scheme 3). Notice that the model for the most hindered ester, namely polymer structure **D** with two γ-substituents, was prepared with two 2-ethylbutyl substituents instead of the 2-methylbutyl substituent, which would arise from the 1,3-rearrangement as depicted in Scheme 2. This was done to avoid centers of asymmetry and as such greatly facilitated the kinetic analysis and also the spectroscopic data. For ease of reference we use a nomenclature system based on the length of the carbon chains substituted on the α-carbon in the carboxylic acid or its derivatives. For example, in this naming scheme acid **3c** corresponds to the 2,6,6-

Scheme 3. Relationship of Model Compounds to Expected Polymer Structures; Nomenclature

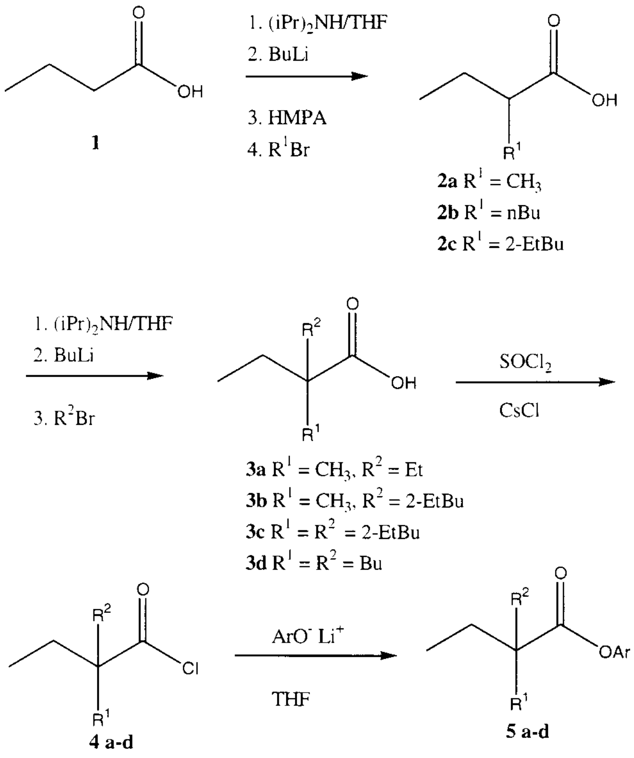


acid, as it has one ethyl substituent and two 2-ethylbutyl substituents on the α-carbon.

The carboxylic acids were synthesized beginning with a carboxylic acid by successive alkylations using lithium diisopropyl amide (LDA) and the appropriate alkyl bromides (Scheme 4). Early synthesis methods for these trialkylacetic acids involved the use of triphenylmethide or potassium amide as a base.[21,22] The use of LDA as a base in THF was originally demonstrated by Creger.[23] Pfeffer[24,25] improved it by using THF/HMPA at 50°, obtaining >90% yields. The solvent effect on these reactions has been reviewed.[26]

In our case, the starting material was *n*-butyric acid, and the alkyl bromides used were methyl bromide, ethyl bromide, or 2-ethylbutyl bromide. The conditions needed for the individual alkylation steps varied because the dilithium derivatives of butyric acid and other primary acids are insoluble in tetrahydrofuran. Hexamethylphosphoramide is used to dissolve dilithium carboxylates after which the alkyl bromide can be added. In the second step, the dilithium derivative of the monoalkylated butyric acid is soluble in tetrahydrofuran, so the reaction is carried out exclusively in that solvent. We introduced other modifications to increase the yield of these reactions, including evaporative removal of THF and diisopropylamine from the reaction mixture to drive the acid−base equilibrium toward the anion before the addition of the alkyl bromide. The separation of pure carboxylic acids was achieved by extraction of appropriate potassium bicarbonate or potassium carbonate solutions, a procedure relying on the different pK_a values of the variously substituted acids. The details of the different syntheses are outlined in the Experimental Section. In addition to the acids depicted in Scheme 3, α,α-di-*n*-butyl-*n*-butyric acid (2,4,4-acid) **3d** was synthesized.

Scheme 4. Synthesis of Model Compounds



The acids were converted to the acyl chlorides by reaction with thionyl chloride. In this simple reaction the sterically crowded environment of the carboxylic acid function manifested itself in quite slow reactions. Heating had to be avoided because it led to decarbonylation of the acyl chloride with formation of the tertiary alkyl chloride as a contaminant.[27] However, at room

Table 2. Crucial ^{13}C NMR and IR Data for the Model Carboxylic Acids and Derivatives

compound	^{13}C NMR C=O shift (δ in ppm, CDCl$_3$)	^{13}C NMR α−C shift (δ in ppm, CDCl$_3$)	IR C=O absorption (cm^{-1})
butyric acid	179		
monoalkylated butyric acid	183−184	44−45	
dialkylated butyric acid	185−186	47−49	1710
acid chloride	179−180	56−57	1785−1795
phenyl ester	175−176	48−49	1650−1655

temperature the reaction could be accelerated by use of cesium chloride catalyst. It acts both as a general base catalyst and reverses ionization of acyl chloride to an acylium ion, which could lose carbon monoxide.

The reactions of the acid chlorides with phenols were also slow, again reflecting the sterically crowded situation of these neosubstituted carboxylic acids and derivatives. We achieved sufficient reactivity by converting the phenol to its lithium salt using 1 equiv of butyllithium. Reaction with the acyl chloride then proceeded to form the phenyl ester model compounds in good yields. For most model reactions, 2-chloro-4-methylphenol was used (CMP esters). The 2,4-dichlorophenyl ester (DCP ester) was also synthesized.

Model amides were synthesized by aminolysis of the aryl esters using the model monoamines, namely *N*,*N*-dimethyl-1,3-propanediamine as a model for a primary amine and *N*-2-aminoethylpiperidine as a model for a secondary amine. The tertiary amine functionalities were introduced in the model amines to mimic the structure of the oligoethylene amines used in the industrial processes.

All of the carboxylic acid and their derivatives were thoroughly characterized by IR and ^{13}C NMR, and the characteristic data are summarized in Table 2. They support the polymer structure assignments.

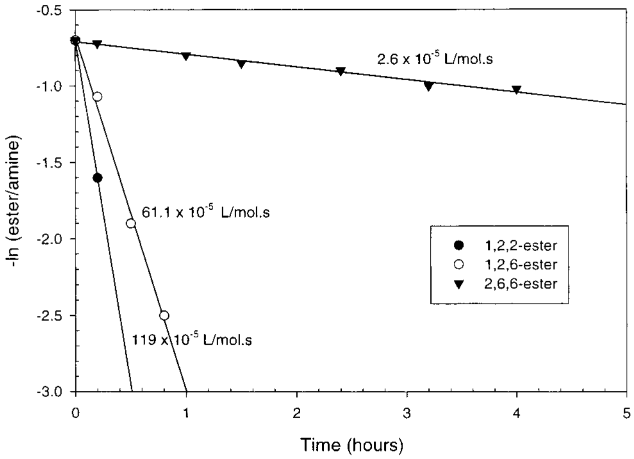
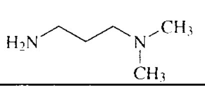
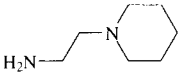
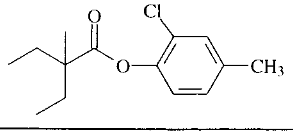
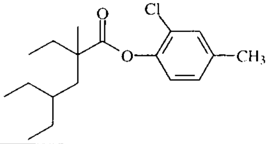
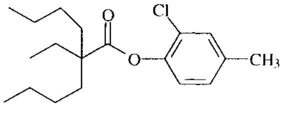
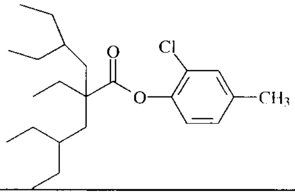


Figure 4. Second-order rate plots of the aminolysis reaction of model compounds: the reaction of 2-chloro-4-methyl rate phenyl esters of several model compounds with 2-aminoethylpiperidine in 2-methylnaphthalene at 200 °C as determined by gas chromatography.

Kinetics of the Reactions of the Model Aryl Esters. The kinetics of aminolysis of the model aryl esters were carried out using two model monoamines, namely *N*,*N*-dimethyl-1,3-propanediamine and *N*-2-aminoethylpiperidine. The reactions were performed in sealed ampules at 200 °C. The solvent was 1-methylnaphthalene, the concentration of ester was 0.91 M, and the amine was used in a 2-fold excess. All reaction components were soluble under these conditions, yielding a homogeneous reaction mixture in all cases. The reaction mixture was analyzed by gas chromatography by following the decrease of ester and appearance of

Table 3. Second-Order Rate Constants for the Reactions of Model Esters with Monofunctional Amines at 200 °C ($k \times 10^3$ L/(mol s))

Ester	Amine 	Amine 
1,2,2-ester 	1.10	1.20
1,2,6-ester 	-	0.60
2,4,4-ester 	0.21	0.31
2,6,6-ester 	0.09	0.03

Scheme 5. Mechanism of Ester Aminolysis

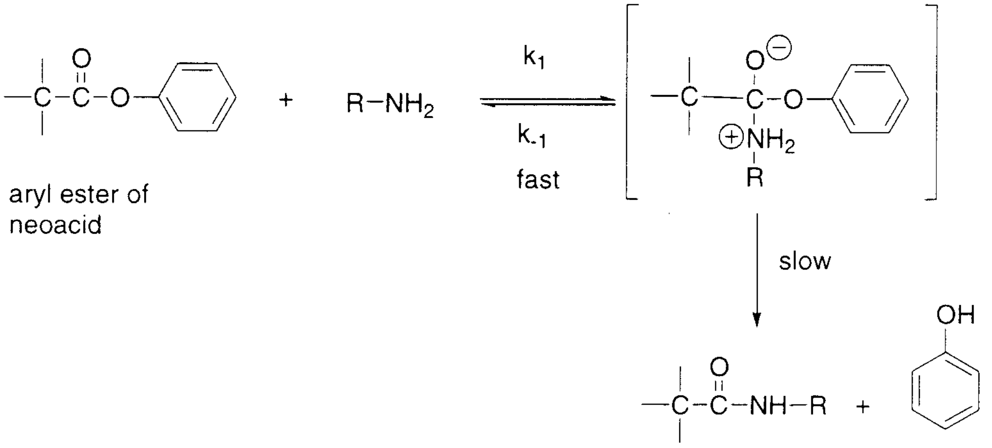


Table 4. Activation Parameters for the Reactions of Model Aryl Esters with Monofunctional Amines[a]

reagents	temp (°C)	ester	E_{act} (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/(K mol))	$\Delta H^{\ddagger}$ (kcal/mol)
1,2,2-ester with *N*,*N*-dimethyl-1,3-propanediamine	100	CTP	6.9	25.9	−52.8	6.1
	100	DCP	7.6	26.7	−53.2	6.9
	100	MTP	7.6	27.4	−55.0	6.9
	100	CMP	9.7	29.0	−53.7	9.0
2,6,6-ester with *N*-2-aminoethyl-piperidine	150	CMP		35.0	−60.7	9.3
	200	CMP		38.0	−60.9	9.2

[a] Solvent: 1-methylnaphthalene.

product with time, using biphenyl as an internal standard. The model amine and leaving group were chosen so that all reactants and products were readily separable by GC.

The reactions were found to be strictly second order, and no drifting rate coefficient was observed. The rate constants were determined with both amines, namely *N*,*N*-dimethyl-1,3-propanediamine (bp 133 °C) and *N*-2-ethylaminopiperidine (bp 186 °C). Four model esters were used in this study at 200 °C. The results are summarized in Table 3.

The rate constants obtained with these model systems fit the range of rate constants generally observed for the polymeric esters, namely between 1.10×10^{-3} and 0.03×10^{-3} L/(mol s). Clearly variations in penultimate monomer account for only a small part of the reactivity differences observed during amination. Carbocation rearrangements, which cause the reactive centers to move further down the polymer chain, are almost certainly implicated. A methyl substituent on the carbocation is thus replaced with a more bulky group increasing steric hindrance about the carbonyl and retarding the reaction kinetics. The difference in the rate constants between the 2,4,4-ester and the 2,6,6-ester is indicative of the effect of the γ-substitution.

The mechanism of ester aminolysis in nonprotolytic solvents has been described extensively in the literature.[28−36] The rates are mainly found to be second-order, first-order each in ester and amine although terms higher order in amine have been observed (Figure 4).

Thermodynamic Activation Parameters and Proposed Mechanism. From various physical organic techniques, researchers have generally concluded that the mechanism of the ester aminolysis involves reversible formation of a zwitterion by addition of the amine to the carbonyl group of the ester.[28−34] This is followed by rate-determining expulsion of the leaving group (Scheme 5).

Both the 1,2,2- and the 2,6,6-CMP esters were studied at various temperatures, because they are respectively the least and the most hindered ester studied. Table 4 represents the thermodynamic activation parameters for these reactions. Noteworthy are the remarkably low values of $\Delta H^{\ddagger}$, varying from 6 to 9 kcal/mol, and the extremely large negative values of $\Delta S^{\ddagger}$, namely more than 50 cal/(K mol). This speaks for a very highly organized zwitterion tetrahedral intermediate. Once the desired conformation of the transition state has been achieved, a smooth low-energy displacement can occur. The increase of rate with increasing electron-attracting substituent in the phenol speaks for a substantial degree of bond cleavage in the transition state. The large steric hindrance due to the type of substitution at the α-carbon and γ-carbons clearly plays a crucial role.

Conclusions. A new AB block copolyhydrocarbon−polyamine polymer has been synthesized by a novel synthesis procedure. The two polymer moieties were linked by a stable sterically hindered amide function. A terminally unsaturated copolymer of ethylene and 1-butene is functionalized to a tertiary carboxylic function using the Koch−Haaf reaction. Boron trifluoride and carbon monoxide in the presence of electron-poor phenols led directly to the tertiary polyhydrocarbon carboaryloxy ester. Deep-seated rearrangements involving 1,3- or 1,5-hydride shifts gave internal as well as the expected terminal carboaryloxy functions. Amination with polyethyleneamine was slow but complete at 200 °C.

The falloff in rate of the polymer amination reactions was ascribed to the sterically crowded internal carboaryloxy functions by matching their reactivity with the appropriate models. The polymer carboaryloxy structures were simulated using small molecule analogues synthesized by alkylation of lithium carboxylates, followed by esterification with electron-poor phenol. The kinetics of their reactions with model monofunctional amines gave excellent agreement with the rate behavior demonstrated by the polymer analogue.

Experimental Section

Representative Synthesis of Ethylene−1-Butene Copolymer (Polymer **1** in Table 1). In a continuous polymerization, ethylene gas was continuously injected into a liquid stream composed of 40 wt % 1-butene and 60 wt % isobutane at a rate sufficient to provide 8.5 wt % ethylene content, based upon the total weight of monomer. The reactant stream containing ethylene, 1-butene, and isobutane was continuously fed into a 568 L, stirred boiling reactor equipped with a water jacket for temperature control at a rate of about 370 kg/h, wherein the vapor formed in the reactor is condensed in an overhead reflux condenser and returned to the reactor. A catalyst solution was prepared by dissolution of solid 1,1-dimethylsilylene bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride into a 10 wt % solution of methylalumoxane in toluene, such that the Al:Zr molar ratio in the solution was 500:1. The catalyst solution was continuously pumped into the boiling reactor at a rate sufficient to provide a Zr concentration of 2.5×10^{-6} M. The temperature of the reactor was maintained at 71 °C, and the reactor pressure was maintained at 170−175 psig (ca. 13 bar). The reactor contents were continuously stirred at a rate of 300 rpm. The reactor residence time was 1 h.

The product stream was continuously fed from the boiling reactor to a quench drum, where it was contacted with an aqueous solution of 350 ppm of NH_4OH. The unreacted monomer, solvent, and quench water were removed from the product by nitrogen stripping. The polymer product was then filtered to remove the catalyst residue. The yield of ethylene−1-butene copolymer was about 70 kg/h. The ethylene content of the copolymer was 22.8 wt %, as determined by proton NMR. According to an analysis by proton NMR, 69.6% of the polymer chains in the polymer were found to have terminal ethylvinylidene unsaturation and 0% were found to have terminal vinyl unsaturation. The polymer had a M_n of 4666 and MWD of 2.3, as determined by gel permeation chromatography using a calibration curve for a polydisperse EB copolymer with 20 wt % ethylene content.

Polymer Properties. Properties of each of the EB copolymers **1**−**5** were measured in accordance with the following procedures. As an additional comparison, certain properties were also determined by these procedures for an isotactic poly(1-butene) with M_n of 1165.

Scattering Factor S_f by Light Scattering.[37,38] EB copolymer (0.5 g) was added to 9.5 g of S150NL mineral oil (5 wt % EB copolymer solution), mixed for approximately 16 h at room temperature, heated and occasionally shaken in an oven at 80−85 °C for several hours, and then filtered at 80−85 °C. About a 5 mL portion of the hot, filtered solution was then immediately placed in the sample chamber of a Brookhaven light scattering goniometer which contains an index matching bath at a temperature of 20 °C. Light from a Spectra-Physics model 124B He−Ne laser (wavelength = 632.8 nm) was directed onto the sample, and the scattered light intensity at a forward scattering angle of 45° was recorded in units of photon counts per second using a Brookhaven BI2000 correlator, where the intensity level was recorded every 10 seconds for 60 min. The results for each of the polymers are collected in Table 1.

Ethylene Sequence Length (ESL) by C-13 NMR.[39,40] EB copolymer product (1 g) was dissolved in 4 g of $CDCl_3$, which also contained 40 mg of chromium acetylacetonate as a paramagnetic relaxation agent. The C-13 NMR spectrum was recorded on a JEOL GSX400 NMR spectrometer at 100 MHz. The following instrument conditions were employed: sample temperature, 30 °C; pulse flip angle, 90°; pulse repetition delay, 3 s; number of acquisitions per spectrum, 8000; and sweep width, 40 000 Hz. Proton decoupling was employed during acquisition but not during recycle delay. Based on an analysis of the spectrum that included the contributions of the terminal groups in the polymer chains, the triad concentrations X_{EEE}, $X_{BEE+EEB}$, and X_{BEB} were obtained on the basis of which ESL was calculated. The results for each of the polymers are collected in Table 1.

Representative Koch−Haaf Carboxylation of EB Copolymer to Polymer Carboxylic Acid. Ethylene−butylene (EB) copolymer (M_n = 3700, about 45 wt % ethylene, 803 g) and 568 g of isooctane were charged to an autoclave, mixed, and heated to 50 °C. $BF_3{\cdot}(H_2O)_{1.1}$ (670 g) was then charged followed immediately by CO, which brought the total autoclave pressure to 2000 psig. The mixture was stirred for 3 h at that temperature and pressure. Pressure was released, and the reaction product was discharged into an aqueous solution containing 600 g of sodium fluoride (NaF), 756 g of water, 302 g of hexane, and 50 g of butanol. The polymer product readily separated from the aqueous phase, was recovered, and dried. The analysis showed 85.1% conversion to neocarboxylic acid.

Representative Koch−Haaf Carboxylation of EB Copolymer to Polymer Aryl Ester. An autoclave was pressured to 199 psig with BF_3 at 50 °C, followed by 301 psig of CO to bring the total pressure to 500 psig. EB copolymer (M_n = 4600, 20 wt % ethylene, 406 g) and 100.6 g of 2,4-dichlorophenol (pK_a = 7.85) at 50 °C were charged to the autoclave and pressured to 1430 psig with CO. The autoclave contents were stirred under these conditions for 2 h and depressurized. The reaction product was stripped to remove BF_3 gas and excess substituted phenol to give a 84.5% yield of EB copolymer aryl ester.

Representative Amination of Polymer Aryl Ester. An ethylene−butene-1 ("EB") copolymer prepared via metallocene−catalyst polymerization of the corresponding monomers (M_n 3300, MWD 2.4, ethylene content 45%, terminal vinylidene 65%) was functionalized via the Koch reaction with carbon monoxide and 2,4-dichlorophenol. The resulting 2,4-dichlorophenyl ester (approximately 100% neoester, 50 g) was mixed with 2.05 g of polyamine HA-2 (Dow Chemical) (approximately 1.2 equiv of primary amine per equivalent of aryl ester) and heated with stirring at 150 °C for 7 h, during which time samples were periodically withdrawn and the conversion of ester to amide measured by the change in the intensity of the ester carbonyl IR band at 1763 cm^{-1}. Carbon-13 NMR analysis showed quantitative conversion of ester to amide. Continuous removal of the phenol over the entire reaction period provided the best results.

General Procedure for the Kinetic Measurements on Model Compounds. To conduct the amidations at high temperatures, 1-methylnaphthalene was chosen as solvent. All the reaction components were soluble in 1-methylnaphthalene and in each case gave a homogeneous reaction mixture. In addition, the signal of 1-methylnaphthalene in the GC chromatogram did not interfere with those of the starting materials and products involved. The corresponding ester and amine (1:2) were dissolved in 1-methylnaphthalene to obtain a 0.91 M solution with respect to the ester. Biphenyl was used as an internal standard. After the start of the reaction, aliquots were taken from the reaction mixture and injected into the GC to monitor the progress of the reaction. The consumption of the ester and the formation of the corresponding monoamide were used to determine the kinetics of the reaction.

The following shows the GC chromatographic conditions used in monitoring the reactions: gas chromatogram, Varian 3300; J&W fused silica megabore column, DB-608; FID detector; 1041 universal injector (Varian); initial column temperature, 50 °C; final column temperature, 250 °C; injector temperature, 250 °C; detector temperature, 300 °C.

Syntheses. The synthesis of the 2,6,6-CMP ester is described in detail as an example of how these neosubstituted esters were synthesized.

*2,6,0-Acid **2c**.* Anhydrous THF (145 mL) and diisopropylamine (28.8 mL, 220 mmol) was added to a dry, nitrogen flushed flask under an atmosphere of nitrogen or argon. *n*-Butyllithium in hexane (88 mL of 2.5 M, 220 mmol) was added to the magnetically stirred solution at such a rate as to maintain the temperature below −10 °C. Butyric acid (8.8 g, 100 mmol) was then added to the cold basic solution, and again the temperature was kept below −10 °C. After 30 min, HMPA

(36 mL, 100 mmol) was added to the milky white solution, which became transparent and light yellow after 5 min of stirring at 0 °C. The solution was stirred for an additional 20 min at 0 °C, and 1-bromo-2-ethyl butane (15.5 mL, 110 mmol) was added at once at 0 °C. The reaction temperature immediately rose to 10 °C. After 3 h of additional stirring at room temperature, the reaction was worked up in the following manner. The solvent was completely removed under vacuum. To the resulting sludge was added 100 mL of water, and the solution was extracted three times with 60 mL portions of cyclohexane. Dilute HCl (10%) was added at 0 °C until the mixture became acidic. The aqueous phase was washed three times with 100 mL portions of cyclohexane. The combined organic layers were washed three times with 100 mL portions of dilute HCl and saturated NaCl solutions. The organic layer was then dried over magnesium sulfate, and the solvent was stripped off.

Yield: 80−90%, pure enough to be used for further alkylation reactions.

^{13}C NMR (CDCl$_3$): δ 183.61 (C=O), 45.04 (C$_q$), 38.22, 35.45, 25.80, 25.50, 24.93, 11.74, 10.60, 10.32 ppm. MS (*m*/*z*): 172 (M$^+$), 143, 125, 115, 101, 88, 85, 73, 55, 43.

2,4-Diethyl-2-(2′-ethylhexyl)hexanoic Acid, 2,6,6-Acid ***3c.*** *n*-Butyllithium (80 mL, 200 mmol, 2.5 M) was added to a solution of diisopropylamine (26 mL, 200 mmol) in 120 mL of tetrahydrofuran cooled at 0 °C under nitrogen. The rate of addition was controlled to prevent the temperature from exceeding −20 °C. After 30 min stirring, 2,6,0-acid (8.6 g, 50 mmol) was added at −30 °C to the LDA solution.

A: The formation of the carbanion was completed by heating the reaction mixture for an additional 2 h at 50 °C. After cooling the reaction mixture, 1-bromo-2-ethylbutane (14.1 mL, 100 mmol) was added rapidly at −40 °C. The exothermicity of the reaction elevated the temperature to −30 °C. The reaction is completed by stirring the mixture for 24−36 h at room temperature. After evaporating off the solvent under reduced pressure, 100 mL of water was added to the residue, and the aqueous solution was extracted three times with 100 mL portions of cyclohexane. The aqueous phase was acidified 10% aqueous hydrochloric acid and extracted with cyclohexane (3 × 100 mL). The separation of the disubstituted product from the monosubstituted starting material was effected by extracting the combined organic layers with saturated potassium carbonate solution, based on difference in pK_a values. The organic layer was dried with magnesium sulfate and evaporated, to give the crude product which is over 99.5% pure as confirmed by GC/MS measurements. Yield: 20−28%.

B: An alternative method to enhance the formation of the carbanion was accomplished by using the equilibrium method. After stirring the carbanion solution at room temperature for 30 min, the solvent and liberated diisopropylamine were removed under vacuum and were recovered in a 2-propanol−dry ice trap. A 40 mL aliquot of fresh distilled dry THF was added to the slurry, and the mixture was cooled to −40 °C. After addition of the alkyl halide, the rest of the procedure is as described above for the 2,6,0-acid synthesis. Yield: 45−52%.

^{13}C NMR (CDCl$_3$): δ 186.08 (C=O), 47.90 (C$_q$), 39.62, 35.81, 26.30, 25.15, 23.39, 10.55, 10.08, 7.85 ppm. MS (*m*/*z*): 256 (M$^+$), 227, 172, 143, 115, 101, 85. IR (KBr, cm^{-1}): 1710 (C=O).

2,4-Diethyl-2-(2′-ethylhexyl)hexanoic Acid Chloride, 2,6,6-Acid Chloride ***4c.*** A mixture of 3.0 g (16.1 mmol) of 2,6,6-acid, 10 mL of thionyl chloride, and 0.27 g (1.6 mmol) of CsCl was stirred at room temperature. The reaction was followed by means of IR spectroscopy and is complete after 18−24 h reaction time. The mixture was filtered and the excess thionyl chloride removed under vacuum, leaving a clean acid chloride which can be used for the esterification reaction. Yield: 80−90%.

^{13}C NMR (CDCl$_3$): δ 179.50 (C=O), 56.09 (C$_q$), 39.80, 35.78, 26.32, 25.17, 23.41, 10.58, 10.04, 8.02 ppm. IR (KBr, cm^{-1}): 2962, 1796 (C=O), 1468.

o-Chloro-p-methylphenyl 2,4-Diethyl-2-(2′-ethylhexyl)hexanoate, 2,6,6-CMP-ester 5c. 2,6,6-Acid chloride (1.02 g, 5 mmol) was added to 3 mL of anhydrous THF, and the reaction mixture was cooled to −40 to −50 °C. After addition of *n*-butyllithium in hexane (2 mL of 2.5 M, 5 mmol), the mixture was stirred for an additional 20 min, and 2-chloro-4-methylphenol (1.2 mL, 10 mmol) dissolved in 2 mL of cyclohexane was added at −40 °C. After further stirring at room temperature for 24−48 h (the more hindered the acid, the longer the reaction time; the reaction mixture is worked up, when the IR shows no acid chloride absorption and only ester absorption), the solvent was removed under vacuum. The residue was taken up in 30 mL of cyclohexane and was washed three times with 30 mL portions of NaOH solution. The combined organic layers were dried over magnesium sulfate. The product was obtained by evaporating off the solvent. Yield: 75−85%.

^{13}C NMR (CDCl$_3$): δ 172.82 (C=O), 144.77, 136.27, 130.68, 128.01, 125.68, 122.98, 49.41 (C$_q$), 39.73, 35.77, 25.95, 25.69, 25.20, 20.58, 10.41, 10.31, 8.31 ppm. IR (KBr, cm^{-1}): 1962, 2876, 1753 (C=O), 1485, 1470, 1044, 1250, 1190, 1100.

Spectroscopic Data on Other Synthesized Compounds. *2-Methylbutanoic Acid, 1,2,0-Acid.* ^{13}C NMR (CDCl$_3$): δ 183.65 (C=O), 40.85 (C$_q$), 26.42, 16.15, 11.33 ppm. ^{1}H NMR (CDCl$_3$): δ 2.38 (hexuplet, 1H), 1.8−1.4 (2m, 2H), 1.17 (d, 3H), 0.9 (t, 3H) ppm.

2-Ethyl-2-methylbutanoic Acid, 1,2,2-Acid. ^{13}C NMR (CDCl$_3$): δ 184.72 (C=O), 46.44 (C$_q$), 31.27, 19.78, 8.75 ppm. ^{1}H NMR (CDCl$_3$): δ 12.3 (br s, 1H), 1.64 and 1.43 (two hexuplets, 4H), 1.13 (s, 3H), 0.85 (t, 3H) ppm. IR (KBr, cm^{-1}): 2980, 2945, 1750, 1600, 1480, 1395, 1220, 1080.

2-Ethyl-2-methylbutanoic Acid Chloride, 1,2,2-Acid Chloride. ^{13}C NMR (CDCl$_3$): δ 179.36 (C=O), 57.09 (C$_q$), 31.27, 20.18, 8.40 ppm. ^{1}H NMR (CDCl$_3$): δ 1.72 and 1.55 (two hexuplets, 4H), 1.13 (s, 3H), 0.82 (t, 3H) ppm.

o-Chloro-p-methylphenyl 2-Ethyl-2-methylbutanoate, 1,2,2-CMP-Ester. ^{13}C NMR (CDCl$_3$): δ 175.10 (C=O), 144.81, 136.67, 130.53, 128.16, 126.19, 123.26, 46.96 (C$_q$), 31.30, 20.57, 20.19, 8.92 ppm. ^{1}H NMR (CDCl$_3$): δ 7.52 (s, 1H), 7.28 (dd, 2H), 2.60 (s, 3H), 1.8−2.3 (2m, 4H), 1.63 (s, 3H), 1.26 (t, 6H) ppm. MS (*m*/*z*): 254 (M$^+$), 142, 107, 85.

2,4-Diethyl-2-methylhexanoic Acid, 1,2,6-Acid. ^{13}C NMR (CDCl$_3$): δ 185.57 (C=O), 46.37 (C$_q$), 43.65, 37.04, 33.25, 27.38, 27.20, 20.57, 11.15, 10.85, 9.28 ppm. IR (KBr, cm^{-1}): 1702 (C=O).

2,4-Diethyl-2-methylhexanoic Acid Chloride, 1,2,6-Acid Chloride. ^{13}C NMR (CDCl$_3$): δ 180.42 (C=O), 56.70 (C$_q$), 42.75, 36.40, 32.83, 26.20, 25.86, 21.02, 10.49, 10.39, 8.58 ppm. IR (KBr, cm^{-1}): 1804 (C=O).

o-Chloro-p-methylphenyl 2,4-Diethyl-2-methylhexanoate, 1,2,6-CMP Ester. ^{13}C NMR (CDCl$_3$): δ 175.52 (C=O), 144.90, 136.57, 130.61, 128.13, 126.14, 123.15, 46.62 (C$_q$), 46.61, 42.66, 36.63, 32.70, 26.86, 26.46, 26.22, 2084, 20.56, 20.49, 10.59, 10.51, 8.93 ppm. MS (*m*/*z*): 310 (M$^+$), 281, 169, 142, 111, 71, 57, 43.

2-Butyl-2-ethylhexanoic Acid, 2,4,4-Acid. ^{13}C NMR (CDCl$_3$): δ 184.73 (C=O), 49.10 (C$_q$), 33.63, 26.79, 26.06, 23.23, 13.97, 8.28 ppm.

2-Butyl-2-ethylhexanoic Acid Chloride, 2,4,4-Acid Chloride. ^{13}C NMR (CDCl$_3$): δ 180.06 (C=O), 60.22 (C$_q$), 33.65, 26.92, 25.95, 23.04, 13.82, 8.17 ppm. IR (KBr, cm^{-1}): 1698 (C=O).

o-Chloro-p-methylphenyl 2-Butyl-2-ethylhexanoate, 2,2,4-CMP-Ester. ^{13}C NMR (CDCl$_3$): δ 175.20 (C=O), 144.81, 136.60, 130.58, 128.14, 126.19, 123.31, 49.71 (C$_q$), 33.71, 26.77, 26.08, 23.21, 20.56, 13.99, 8.29 ppm.

Acknowledgment. The authors gratefully acknowledge the Exxon Paramins Division for support and permission to publish this work.

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MA001947O