

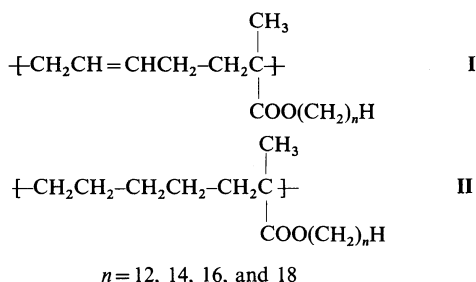
Synthesis, Structure, and Thermal Properties of Widely-Spaced Comb-Like Polymers

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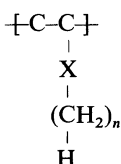
ABSTRACT: Alternating copolymers of butadiene and long alkyl methacrylates **I** and their hydrogenated copolymers **II** were synthesized, characterized and designated as widely-spaced comb-like polymers.



A differential scanning calorimetry study of these copolymers indicated that their alkyl side chains could crystallize in the same order as those of poly(alkyl methacrylates).

KEY WORDS Comb-Like Polymer / Widely-Spaced Comb-Like Polymer / Butadiene / Methacrylate / Long Alkyl Group / Alternating Copolymer / Hydrogenation / Differential Scanning Calorimetry / Crystallization

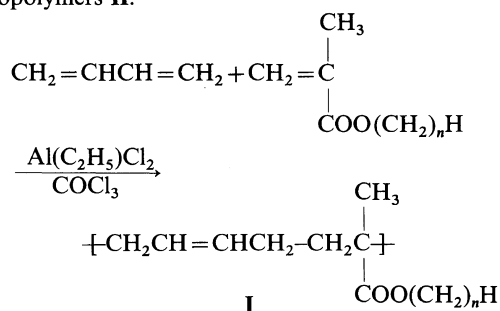
Macromolecules whose repeating units have long side chains (generally an alkyl group) are denoted as comb-like polymers¹ and have been intensively studied in recent years owing to their intermediate place between linear and branched polymers.²

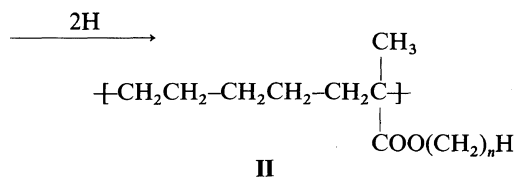


These comb-like polymers are known to crystallize through alkyl side chain packing independently of the stereoregularity of the main chain. This was first recognized by Greenberg and Alfrey³ who reported the ability of atactic poly(alkyl acrylates) and poly(alkyl methacrylates) to form crystalline phases made up of alkyl side chains rather than main

chains. So far, such macromolecules as poly(1-alkenes),⁴ poly(alkyl vinyl ethers),⁵ poly(vinyl alkanoates),⁶ poly(alkylstyrenes),⁷ have been studied.

This paper deals with the synthesis, structural characterization and a differential scanning calorimetry study of alternating butadiene-long alkyl methacrylate copolymers **I** and their hydrogenated copolymers **II**.





In these copolymers, the long alkyl side chains appear on every six main chain carbon atoms and therefore are designated as widely-spaced comb-like polymers (Figure 1). Our interest was directed to finding out whether these widely-spaced side chains, with intervening seven carbon atoms, crystallize.

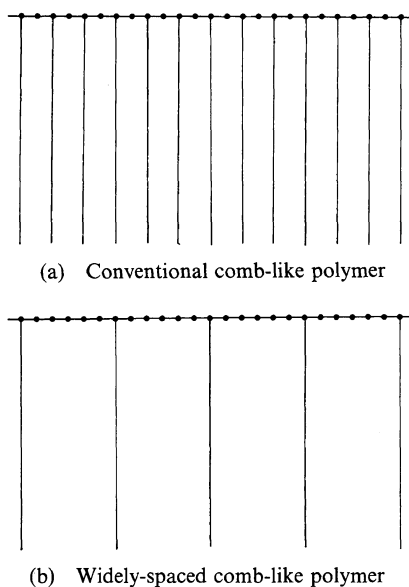


Figure 1. Schematic diagrams of (a) conventional and (b) widely-spaced comb-like polymers.

Overberger *et al.*⁸ studied the glass-transition temperature of poly(2-alkyl-1,3-butadienes) in an attempt to improve the low temperature flexibility of these rubbers. In this series of polymers, alkyl side chains appear on every four carbon atoms. Because the alkyl groups studied were not long enough (heptyl and decyl), they could observe only the glass-transition but not melting temperatures.

EXPERIMENTAL

Monomers

Butadiene extra pure grade was commercially

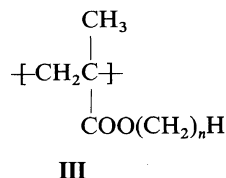
obtained. Alkyl methacrylates were prepared by the alcoholysis of methyl methacrylate with higher alcohols in the presence of *p*-toluenesulfonic acid as the catalyst and a trace amount of hydroquinone as the inhibitor. They were purified by distillation under vacuum in the presence of the inhibitor, and characterized by their boiling points, infrared (IR) and ¹H nuclear magnetic resonance (NMR) spectra. Dodecyl, tetradecyl, hexadecyl, and octadecyl methacrylates were synthesized.

Other Reagents

Ethylaluminum dichloride from Ethyl Corp. was distilled under vacuum and dissolved in toluene (50 vol%). Extra pure vanadyl chloride was dissolved in hexane as received (0.25 mol dm⁻³). Extra pure *p*-toluenesulfonylhydrazide was recrystallized from ethanol.

Polymerization

The synthesis of alternating butadiene-alkyl methacrylate copolymers was carried out essentially by the method in our previous paper using the hydrogenated alternating butadiene-methyl methacrylate copolymer.⁹ A mixture of butadiene, an alkyl methacrylate, the ethylaluminum dichloride solution (equimolar to alkyl methacrylate), and the vanadyl chloride solution (1/40 molar to ethylaluminum dichloride) in a test tube was occasionally shaken for several hours until it solidified in an ice-water bath. The mixture was then poured into methanol containing 1 vol% of concentrated hydrochloric acid to precipitate the alternating copolymer I. It was purified by repeated reprecipitations from the benzene solution into acetone. Poly-(alkyl methacrylates) (homopolymers III) were obtained for comparison by warming alkyl methacrylate monomers in equivolume toluene with α,α' -azobisisobutyronitrile (1 mol%) at 60°C.



Hydrogenation

Platinum black-catalyzed hydrogenation, by either atmospheric or high pressure hydrogen, was very slow for long alkyl side chain copoly-

mers **I**. Hydrogenation by *p*-toluenesulfonylhydrazide¹⁰ gave good results. To a refluxing toluene solution of a copolymer **I**, 2 equivalents of *p*-toluenesulfonylhydrazide were added portionwise. After 5 h refluxing, the solution was poured into a large volume of methanol to precipitate the hydrogenated copolymer **II**. The residual unsaturation in the copolymer was checked by ¹H NMR spectrum and was again reacted with 2 equivalents of the reagent to complete the hydrogenation. The copolymer yield was almost quantitative.

Measurement

IR spectra were recorded on a JASCO IR-E spectrometer. ¹H and ¹³C NMR spectra were taken on a Hitachi R-20B operating at 60 MHz and a Varian XL-200 at 50 MHz, respectively, in deuteriochloroform solutions with hexamethyldisiloxane (HMDS) as the reference. X-Ray diffraction patterns were recorded with film samples using Ni-filtered Cu-K α radiation on a Rigaku-Denki RAD II diffractometer. Film samples were obtained by casting from the polymer solutions in tetrahydrofuran on slide glass. Differential scanning calorimetry (DSC) was determined on a Rigaku-Denki Thermoflex provided with a low temperature unit. About a 2 mg sample was taken (20 mg for C₁₂ polymers) in an aluminum pan covered with a lid. Both the heating and cooling rates were 5 °C min⁻¹ throughout. Gel-permeation chromatography was run on a Toyo-Soda HLC-802UR with two 2-ft GMH columns in tetrahydrofuran. The columns were calibrated with a set of linear narrow molecular weight polystyrenes.

RESULTS AND DISCUSSION

Characterization of the Copolymer Structure

Table I shows the yields and molecular weights of the copolymer **I**, **II**, and homopolymer **III** samples used in the DSC study. The molecular weight distributions were polydisperse and the molecular weights were estimated from the gel-permeation chromatogram peak tops. An example is shown in Figure 2.

Figures 3 and 4 show the IR and ¹H NMR spectra of the alternating butadiene-octadecyl methacrylate copolymer (copolymer **I**-C₁₈), its hydrogenated copolymer (copolymer **II**-C₁₈), and poly(octadecyl methacrylate) (homopolymer **III**-

Table I. Synthesis of comb-like polymers

Polymer	Yield	Molecular weight ^a
	%	$\times 10^{-4}$
I -C ₁₂	68	c
II -C ₁₂	b	4
III -C ₁₂	63	30
I -C ₁₄	52	c
II -C ₁₄	b	9
III -C ₁₄	65	30
I -C ₁₆	29	c
II -C ₁₆	b	30
III -C ₁₆	88	9
I -C ₁₈	21	c
II -C ₁₈	b	50
III -C ₁₈	72	60

^a By GPC peak tops.

^b Quantitative.

^c Not determined.

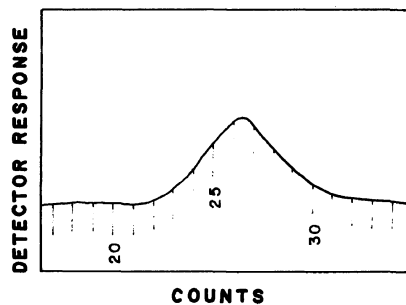


Figure 2. GPC chromatogram of hydrogenated alternating butadiene-octadecyl methacrylate copolymer **II**-C₁₈. A differential refractometer detector was used.

C₁₈). Other polymers having C₁₂–C₁₆ alkyl side chains showed essentially the same spectra as these, because of the trivial difference in the number of carbon atoms in the side chains.

The alternating structure of copolymers **I** and hence the periodic structure of copolymers **II**¹¹ could be confirmed by the following facts. (1) In the ¹H NMR spectra of copolymers **I**, the peak intensity ratios of the α -CH₂ of alkyl side chains in methacrylate units (4.00 ppm) to the –CH=CH– of butadiene units (5.30 ppm) were approximately 1 : 1; this was the case for all the copolymers obtained from experiments with various monomer feed ratios. (2) All of the various alternating butadiene-methacrylate ester copolymers synthesized in our

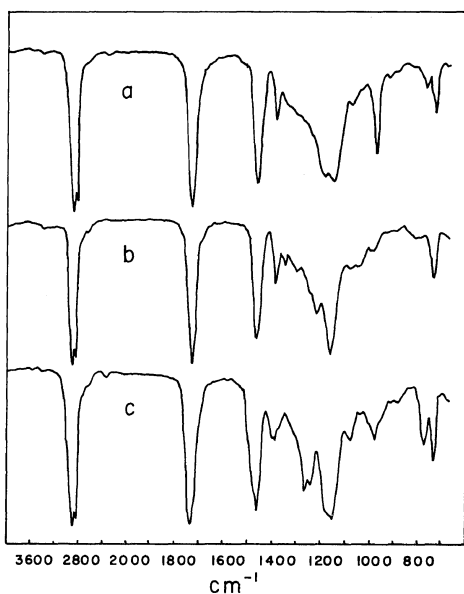


Figure 3. IR spectra of (a) alternating butadiene-octadecyl methacrylate copolymer **I**-C₁₈, (b) its hydrogenated copolymer **II**-C₁₈, and (c) poly(octadecyl methacrylate) **III**-C₁₈. Spectra were taken for films cast on rock salt plates.

previous paper¹² were found to have the proposed structures on the basis of a ¹³C NMR study of their hydrogenated copolymers. (3) The proton noise decoupled and INEPT (Intensive Nuclear Enhancement through Polarization Transfer¹³) ¹³C spectra of **II**-C₁₈ in Figure 5 along with data in Table II summarizing the ¹³C chemical shifts of the skeletal carbon atoms of various hydrogenated butadiene-methacrylate ester copolymers make it possible to assign several peaks to the skeletal carbon atoms of **II**-C₁₈, as shown in Figure 5. These peaks are so sharp and single that they indicate a high sequential purity of the hydrogenated copolymer and hence the parent alternating copolymer.

Thus we have two types of widely-spaced comb-like polymers, **I** and **II**, and conventional comb-like polymers, **III**, with C₁₂, C₁₄, C₁₆, and C₁₈ alkyl side chains.

DSC Curves of Conventional Comb-Like and Widely-Spaced Comb-Like Polymers

At first, the DSC measurement was carried out using a heating mode. While homopolymers **III** showed single endothermic melting peaks at the

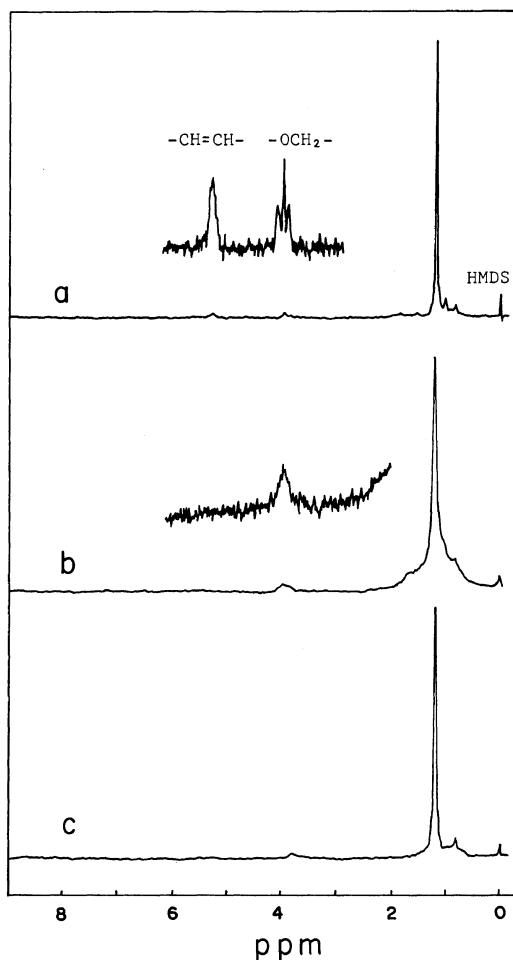


Figure 4. ¹H NMR spectra of (a) alternating butadiene-octadecyl methacrylate copolymer **I**-C₁₈, (b) its hydrogenated copolymer **II**-C₁₈, and (c) poly(octadecyl methacrylate) **III**-C₁₈. Spectra were obtained at 60 MHz in deuteriochloroform with HMDS as a reference.

temperatures reported in the literature,³ copolymers **I** and **II** generally showed two melting peaks. This is probably due to crystal reorganization during the heating process. Therefore, studies were carried out using a cooling mode.

A sample was first heated to and maintained for 5 min at about 30 degrees higher than its melting temperature. The cooling DSC curve was then recorded. Single exothermic freezing peaks were observed for all polymers at temperatures several degrees lower than the corresponding melting

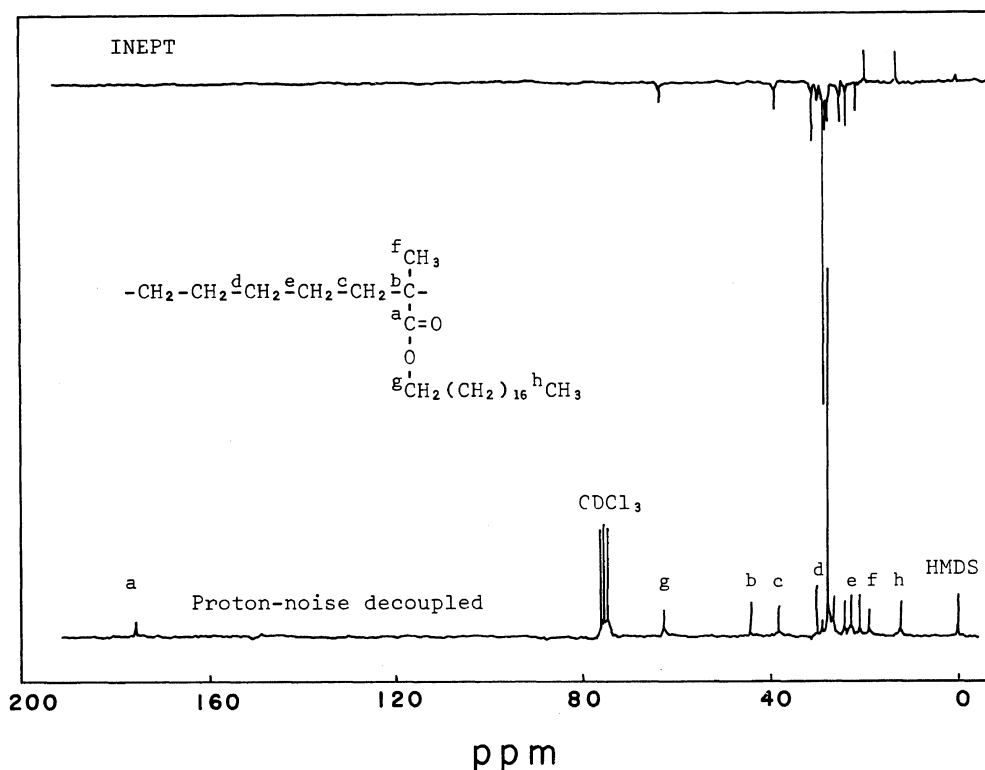
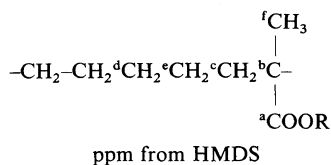


Figure 5. Proton noise decoupled and INEPT ^{13}C spectra of the hydrogenated butadiene-octadecyl methacrylated copolymer II. Spectra were obtained at 50 MHz in deuteriochloroform with HMDS as a reference. The INEPT spectrum shifted slightly downfield for better illustration.

Table II. ^{13}C NMR Chemical shift of the skeletal carbons of various hydrogenated butadiene-methacrylate esters copolymers,



R	^a C	^b C	^c C	^d C	^e C	^f C
Methyl	176.31	44.04	37.60	28.71	22.56	19.19
Ethyl	175.52	43.86	37.56	28.77	22.53	19.10
Isopropyl	174.93	43.75	37.58	28.85	22.52	19.01
Phenyl	173.97	44.33	37.61	28.75	22.66	19.12
Benzyl	175.25	44.03	37.63	28.73	22.57	19.03

Tetradecyl	175.53	44.00	37.83	28.92	22.71	19.02
Octadecyl	175.51	44.00	37.86	28.93	22.72	19.01

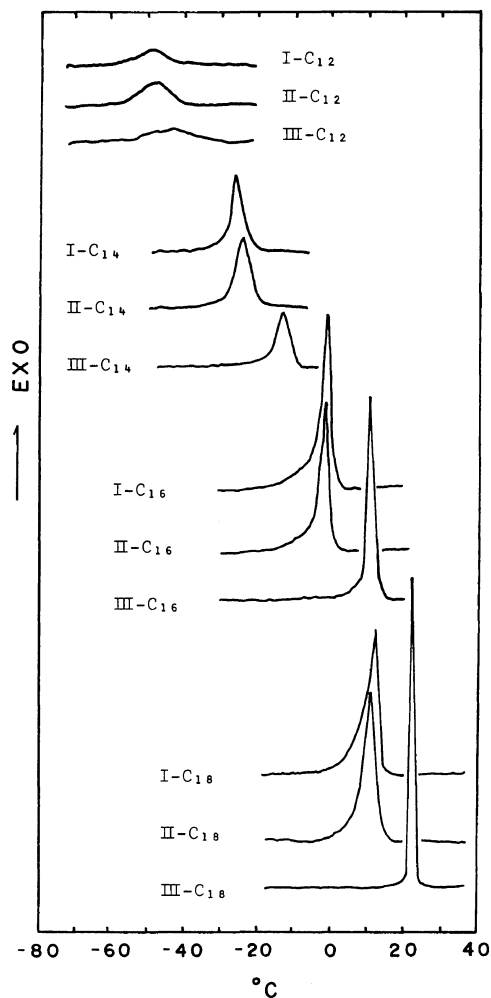


Figure 6. DSC curves for the widely-spaced comb-like polymers **I** and **II** and the conventional comb-like polymers **III**. The cooling rate was $5^{\circ}\text{C min}^{-1}$.

peaks. (In our previous papers,^{9,12} **I** and **II** type polymers with methyl and benzyl ester groups showed melting peaks owing to the periodic structure of their main chains. But the polymers with ethyl, isopropyl, and phenyl ester groups did not do so in spite of their identified periodic structures. Copolymers **I** and **II** in this paper may possibly be of the latter group and showed only single peaks.) The results are compiled in Figure 6. In general, as the number of carbon atoms in the alkyl side chains increases from 12 to 18, the freezing peaks of copolymers **I** and **II** as well as homopolymers **III** shift to higher temperatures and become sharper

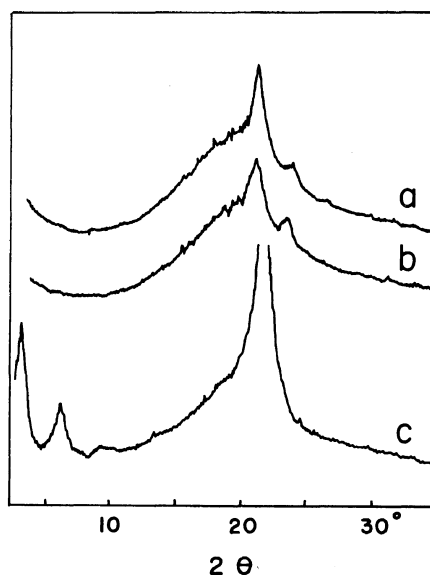


Figure 7. X-Ray diffraction patterns of (a) alternating butadiene-octadecyl methacrylate copolymer **I-C₁₈**, (b) its hydrogenated copolymer **II-C₁₈**, and (c) poly(octadecyl methacrylate) **III-C₁₈**.

and stronger. Copolymers **I** and **II** showed somewhat broader peaks at lower temperatures than homopolymers **III** with the same alkyl side chains.

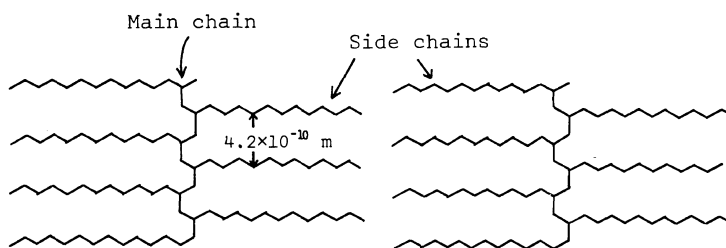
Thus, the long alkyl side chains in the widely-spaced comb-like polymers **I** and **II** are considered to crystallize like those of the conventional comb-like polymers **III** in spite of the intervening seven main chain carbon atoms between them. The freezing temperatures, T_f , determined from the peak tops, are summarized in Table III.

X-Ray Diffraction Patterns

Figure 7 shows the X-ray diffraction patterns of copolymers **I** and **II** and homopolymer **III**. All samples showed peaks at about $2\theta = 21^{\circ}$, indicating 4.2×10^{-10} m spacings. On the basis of a detailed study of the conventional comb-like polymers for which good diffraction patterns were obtained, a peculiar layered structure made up of parallel alkyl side chains arranged on both sides of the main chain has been proposed (Figure 8).² In this structure, the spacing between two neighboring alkyl side chains is 4.2×10^{-10} m. For the widely-spaced comb-like polymers **I** and **II**, a similar packing of alkyl side chains may be possible. The packing may be like that depicted in Figure 1(b). The conformations of

Table III. Thermal properties of comb-like polymers

Polymer	Freezing temperature	Heat of crystallization	Number of crystallizing CH ₂ group
	T_f		
	°C	kcal repeating unit ⁻¹ mol ⁻¹	N
I-C ₁₂	-48	0.46	0.6
II-C ₁₂	-48	0.63	0.9
III-C ₁₂	-42	0.38	0.5
I-C ₁₄	-26	1.97	2.7
II-C ₁₄	-25	2.52	3.4
III-C ₁₄	-13	1.40	1.9
I-C ₁₆	-1	3.96	5.4
II-C ₁₆	-2	4.62	6.3
III-C ₁₆	11	2.95	4.0
I-C ₁₈	12	5.49	7.5
II-C ₁₈	12	6.01	8.2
III-C ₁₈	23	4.12	5.6


Figure 8. A proposed structure for conventional comb-like polymers.²

the main chains should be modified to a small extent so as to accommodate the above spacings.

IR Spectra in the 720 cm⁻¹ Region

Chapman¹⁴ pointed out the correlation between the appearance of bands associated with the CH₂ rocking mode in the 720 cm⁻¹ region of the IR spectra of crystalline long alkyl chain compounds and the type of alkyl chain packing. Compounds showing two peaks at 727 and 719 cm⁻¹ are of the orthorhombic type packing and those showing a single bands at 720 cm⁻¹ are of the hexagonal type packing. Shibaev *et al.*¹⁵ showed that homopolymers **III** as well as poly(alkyl acrylates), poly(alkyl vinyl ethers), and poly(vinyl alkanoates) all crystallized in hexagonal packing (in accordance with X-ray studies) as characterized by a single absorption band at 720 cm⁻¹. In Figure 3 copolymers **I** and **II**

show single bands at 720 cm⁻¹, indicating that their long alkyl side chains are of the hexagonal type packing and certainly not of the orthorhombic type packing.

Number of Crystallizing CH₂ Groups

Table III also shows the heats of crystallization, ΔH_f , estimated from the DSC peak areas, and the number of crystallizing CH₂ groups in the side chains, N , for copolymers **I** and **II** and homopolymers **III**. The quantity, N , was calculated by dividing ΔH_f by the heat of fusion per CH₂ of *n*-alkanes in the hexagonal packing (735 cal CH₂⁻¹ mol⁻¹¹⁶). No correction was made for any contribution from the end groups.

As shown in Figure 9, the N values increase as the number of carbon atoms in the side chains increase for copolymers **I** and **II** and homopolymers **III**. The

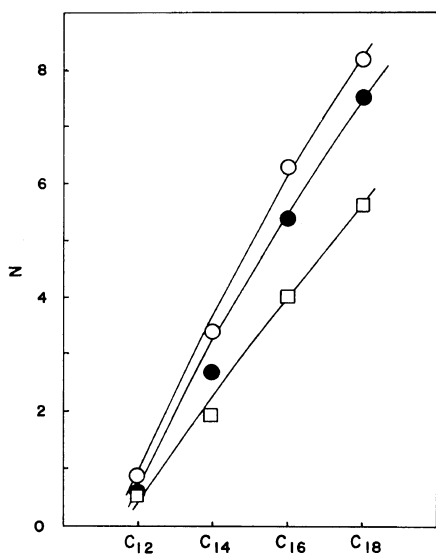


Figure 9. The relationship between the number of crystallizing CH_2 groups, N , and the length of alkyl side chain. Filled circles, copolymers I; open circles, copolymers II; and squares, homopolymers III.

N values for copolymers I and II are similar and somewhat larger than those for the corresponding homopolymers III. That is to say, in spite of intervening seven carbon atoms in the main chain, the alkyl side chains of widely-spaced comb-like polymers can crystallize to a greater extent than conventional comb-like polymers. This is because the main chains of copolymers I and II are more flexible than those of homopolymer III, as suggested by their tensile properties¹² and allow the side chains to come closer to each other and crystallize. However, though the total number of crystallizing CH_2 groups is somewhat larger for widely-spaced comb-like polymers, the length of crystallizing CH_2 groups is not uniform and broad peaks are observed in Figure 6. The lower T_f values for I and II than that for III as shown in Figure 6 and Table III may result from the larger entropy of melting for I and II. In the melt phase, the alkyl side chains of I and II can move more freely than those of III, because of the wider spaces.

Conclusions

Two types of widely-spaced comb-like polymers whose long alkyl side chains appear on every six main chain carbon atoms were synthesized and characterized. A DSC study revealed that the alkyl side chains can crystallize as in the case of conventional comb-like polymers.

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