and Kwart[1] found that no measurable amount of polymerization took place up to the end of the induction period. For this reason they were unable to determine the value of k_x/k_p. However, with methyl methacrylate a small but measurable amount of polymerization does take place prior to the end of the induction period, and after the end of this period the rate is found, within the experimental error, to be unretarded. The magnitude of k_x/k_p was obtained by plotting α *vs.* ln $(1 - (t/T))$ for the three runs with picrylhydrazyl; a typical plot is shown in Fig. 6. In addition the rate of decomposition of the initiator was calculated from the length of the induction period. The results obtained with picrylhydrazyl are summarized below in Table III.

From the average value of k_x obtained it is apparent that the hydrazyl is approximately 400 times more reactive toward methyl methacrylate radical than benzoquinone, the most active of the other terminators studied.

TABLE III

EFFECT OF DIPHENYLPICRYLHYDRAZYL ON METHYL METHACRYLATE POLYMERIZATION

Run	(AIBN) $\times 10^2$ (moles/l.)	(DPPH) $\times 10^4$ (moles/l.)	k_{df} for AIBN (sec.$^{-1}$), calcd. from induction period	k_x/k_p
2	2.50	5.4	6.9×10^{-7}	2100
3	2.33	2.6	7.9×10^{-7}	2000
4	3.16	4.2	7.2×10^{-7}	2000

Av. value of k_x = 920,000

A similar study of the behavior of terminators in methyl acrylate polymerization will be the subject of a future paper.

Acknowledgments.—The author wishes to thank Drs. T. G Fox and S. Gratch of these laboratories for their helpful comments and advice; the author is also indebted to Mr. C. A. Cooper for his assistance with the experimental portion of this investigation.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Side Chain Crystallization of *n*-Alkyl Polymethacrylates and Polyacrylates[1]

BY SIDNEY A. GREENBERG[2] AND TURNER ALFREY

RECEIVED MAY 17, 1954

In this study of side chain crystallinity, methacrylate and acrylate monomers, with *n*-alkyl groups containing from 12 to 18 carbon atoms, were synthesized, polymerized and copolymerized; dilatometric measurements were made on these polymers to determine the changes in specific volume with temperature and time; spacings were obtained from Debye–Scherrer patterns taken at small and wide angles. The following results were noted: the specific volume–temperature plots were S-shaped, typical of first-order transitions; crystallization was rapid and accompanied by very little supercooling; melting ranges were short except for the mixed long chain copolymers; long and short spacings were found in the X-ray patterns. The melting ranges of the polymers did not depend on the temperature of the cooling bath.

Introduction

In this paper there is described an investigation of the side chain crystallinity found in polymethacrylates and polyacrylates with *n*-alkyl groups from 12 to 18 carbon atoms in length. These crystalline polymers differ from crystalline polyethylene[3a] and natural rubber[3b] in that the crystallites are made up of the *n*-alkyl groups which extend from the backbone of the molecules, rather than of segments of the backbone itself.

Rehberg and Fisher[4] prepared a series of the polyacrylates and methacrylates and found that the brittle points of these polymers, beginning with polydodecyl methacrylate and polyoctyl acrylate, increase with the lengths of the *n*-alkyl groups. This increase in brittle points has been attributed[5] to the higher melting points of the polymers with longer alkyl groups.

Very little appears in the literature on the subject of side chain crystallinity. Barrer[6] predicted crystallization of long side chains, and in the same discussion Crisp stated that the properties of polyoctadecyl methacrylate surface films were affected by the interactions of the long side chains. Wiley and Brauer[7] found breaks in the index of refraction *versus* temperature curves of polyhexadecyl and polytetradecyl acrylates and of polyhexadecyl methacrylate. These breaks occurred in the same temperature ranges as the brittle points of the polymers. Similarly, polyvinyl palmitate and stearate and the copolymers of vinyl stearate and vinyl acetate were prepared by Swern and Jordan[8] and are hard wax-like solids, which indicates that the side chains have probably crystallized.

In this study of the structure and crystalline–amorphous equilibrium of the various polymers, the following experimental work was carried out.

(1) The long chain (12 to 18 carbon atoms) acrylate and methacrylate monomers were synthesized by the alcoholysis of methyl acrylate and methyl methacrylate.

(2) Monomers, thus synthesized, were polymerized in bulk, emulsion or solution, and co-

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(1) Abstracted in part from a dissertation presented by Sidney A. Greenberg to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Summaries of this work were presented before the Division of Polymer Chemistry, American Chemical Society Meeting, Chicago, Illinois, September, 1950.

(2) Johns-Manville Research Center, Manville, New Jersey.

(3) (a) E. Hunter and W. G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945); (b) L. A. Wood and N. J. Bekkedahl, *J. Research Natl. Bur. Standards*, **36**, 489 (1946).

(4) C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

(5) H. S. Kaufman, A. Sacher, T. Alfrey and I. Fankuchen, THIS JOURNAL, **70**, 3147 (1948).

(6) R. M. Barrer and D. J. Crisp, *Trans. Faraday Soc.*, **38**, 431 (1942).

(7) R. H. Wiley and G. M. Brauer, *J. Polymer Sci.*, **3**, 647 (1948).

(8) D. Swern and E. F. Jordan, THIS JOURNAL, **70**, 2334 (1948).

TABLE I

REACTION MIXTURES

Expt. no.	Polymer type[a]	Monomer 1 no. of C atoms in alkyl group	g.	Monomer 2 no. of C atoms in alkyl group	g.	Monomer 1, mole %	CCl_4, g.	Benzoyl peroxide, g.	Reaction time, days
				Emulsion[b]					
1	M.P.	18	15			100		0.5	5
2	M.P.	14	20			100		.06	15
3	M.P.	12	20			100		.03	1
4	A.P.	14	50			100		1.0	2
5	M.C.	16	10	1	3.23	50		0.03	0.6
6	M.C.	14	20	1	7.00	50		.06	2
7	M.C.	18	10	14	8.83	50		.5	5
8	M.C.	12	10.6	Commercial monomer mixture				.08	0.6
9	A.C.	18	20	1	1.85	75		.3	1
10	A.C.	18	20	1	5.57	50		.3	1
11	A.C.	16	15	1	4.36	50		.5	5
				Bulk					
12	M.P.	18	3			100		0.05	1
13	M.P.	16	3			100		.05	4
14	M.P.	14	30			100		.70	4
15	A.P.	18	25			100		.80	4
16	A.P.	16	21.4			100		.40	3
17	A.P.	12	20			100		.30	3
18	M.C.	18	10	1	2	59.5		.15	3
19	M.C.	18	10	1	7	37.0		.15	4
20	M.C.	18	10	16	10	50.0		.40	3
				Solution					
21	M.C.	18	10	1	1.3	69.5	17	0.15	4
22	M.C.	18	40	1	12.0	50.0	65	.80	3
23	M.C.	18	10	1	3.0	50.0	18	.03	2

[a] M.P. = methacrylate polymer, A.P. = acrylate polymer, M.C. = methacrylate copolymer, A.C. = acrylate copolymer. [b] In addition to the listed components each mixture contained 0.2 g. of Triton K-60, 2.5 ml. of water, 0.5 ml. of hydrogen peroxide except in experiment no. 4 in which case twice these amounts were used.

polymerized with short-chain (methyl) and long chain monomers.

(3) The melting ranges and rates of crystallization of the polymers and copolymers were studied by measuring the changes in specific volumes with temperature and time.

(4) Debye–Scherrer wide and small angle diagrams were obtained to determine spacings and repeat distances (along axis of stress) of the crystallites.

Experimental

Materials.—The methyl methacrylate and acrylate monomers were obtained from Rohm and Haas, and were purified by distilling under vacuum. These monomers were treated with alcohols obtained from Humphrey–Wilkenson, Inc., New Haven, Conn., which were used as received. A commercial-grade dodecyl methacrylate, prepared from a mixture of alcohols, was secured from Rohm and Haas; inhibitor was removed from this monomer by washing it with a dilute sodium hydroxide solution. This monomer contained a *n*-alkyl mixture of the following composition: hexyl, 3%; dodecyl, 61%; tetradecyl, 23%; hexadecyl, 11%; and octadecyl, 2%.

Preparation of the Monomers.—The higher *n*-alkyl methacrylate and acrylate monomers used in this study were prepared by the procedure of Rehberg and Fisher.[9] In this procedure methyl acrylate and methacrylate monomers are alcoholized by long chain alcohols. The alcoholysis is catalyzed by sulfuric acid, and polymerization of the monomers is inhibited with *p*-*t*-butylcatechol. Monomers prepared in this manner were purified by distillation under vacuum.

Some difficulty was encountered in the preparation of octadecyl methacrylate monomer. Polymerization took place during the alcoholysis reaction and also during the distillation of the product. The following steps were taken to avoid polymerization: (1) a column packed with copper gauze was found to best inhibit polymerization during the alcoholysis reaction, and (2) in order to avoid prolonged heating of the monomers during distillation, a small amount of monomer was added to a 500-ml. Claisen flask fitted with a dropping funnel, and as this monomer was vacuum distilled, more was added to the flask.

Polymerization Methods.—Some of the monomers were polymerized by the emulsion technique previously used by Rehberg and Fisher.[9] In this procedure, polymerization is catalyzed by benzoyl peroxide and hydrogen peroxide, and Triton K-60 is used as the emulsifying agent. Polymerizations were also carried out in a solution of carbon tetrachloride (a chain transfer agent) and in bulk. In these reactions, benzoyl peroxide was the catalyst employed. Table I lists the reaction mixtures from which the copolymers and polymers were prepared.

The monomers and catalyst were placed in tubes or bottles which were subsequently sealed, and polymerizations were carried out in a 100° bath. After polymerization was complete, the polymers were purified by dissolving them in benzene, dioxane or ether and then precipitating them in methanol. This procedure was repeated four times. Many of the polymers can be obtained as fine powders by precipitating them in methanol, which has been cooled with Dry Ice. It was found that the frozen benzene technique[10] can be used successfully on copolymers of hexadecyl or octadecyl methacrylate and methyl methacrylate.

Dilatometry.—The rates of crystallization and melting ranges of the polymers were obtained from the changes in

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(9) C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1203 (1944).

(10) F. Lewis and F. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

TABLE II

EXPERIMENTAL RESULTS FROM SPECIFIC VOLUME MEASUREMENTS

Expt. no.	Monomeric units in polymer $M_1 - M_2$ No. of carbon atoms in *n*-alkyl groups	M_1 in monomer mixture, mole %	Specific vol. change in melting		Melting range, °C.	No. of degrees in range, °C.	T_m (m.p.), °C.	Brittle point,[4] °C.
			%	Cc./g.				
	Methacrylates							
12	18	100	3.7	0.039	33–34	1	34	...
1	18	100	3.0	.032	33–35	2	34	...
13	16	100	2.5	.028	16–21	5	20	15
14	14 (B.P.)[a]	100	1.7	.016	(−3)–0	3	− 2	− 6
2	14 (E.P.)[a]	100	1.8	.019	...	..	...	...
3	12	100	2.1	.021	(−34)–(−36)	2	−34	−34
	Acrylates							
15	18	100	6.1	.063	39–43	4	42	...
16	16	100	6.9	.073	32–33	1	33	35
4	14	100	4.5	.045	21–22	1	22	22
17	12	100	1.6	.018	0–4	4	2	− 2
	Methacrylate copolymers							
21	18–1	69.5	2.6	.035	24–29	5	28	
18	18–1	59.5	...	...	29–33	4	32	
22	18–1	50	1.5	.014	27–34	7	30	
19	18-1	37	No melting curve					
5	16–1	50	...	..	19–29	10	25	
6	14–1	50	0.7	.007	(−1.5)–2	3	0	
	Acrylate copolymers							
9	18–1	75	...	...	39–44	5	42	
10	18–1	50	6.7	.068	38–42	4	42	
11	16–1	50	...	...	20–27	7	25	
	Mixed long chain methacrylate copolymers							
20	18–16	50	3.9	.040	14–24	10	22	
7	18–14	50	3.6	.037	6–26	20	18	
8	12	Commercial monomer mixture	1.3	.014	(−23)–(−14)	9	−16	

[a] E.P. = emulsion polymerized; B.P. = bulk polymerized.

specific volumes with temperature and time. This was the method employed by Wood and Bekkedahl[3] to investigate crystallization in natural rubber, and the dilatometric procedure in this study was modelled after the one used by them. In this procedure a polymer of known specific volume (25°) with mercury as a confining fluid is placed in a dilatometer. From the changes in the height of the mercury, the specific volumes of the polymer can be calculated.

Several modifications were made in the dilatometer used by Wood and Bekkedahl to adapt it to measure specific volume changes in methacrylate and acrylate polymers. A dilatometer used in this study consisted of two parts: (1) a cup with a 10/30 ground-glass female joint, and (2) a calibrated capillary with a 10/30 ground-glass male joint. In each case, the procedure for placing the polymers and mercury into the dilatometers was the same. The polymer wss inserted into the cup, which was then placed into a 70° oven. At this temperature, the polymer spread evenly over the bottom of the cup. To remove any volatile impurities from the polymer, it was subjected to a vacuum of 2 mm. pressure at room temperature for at least 24 hours. After the impurities were removed, the cup and capillary were joined under mercury. To prevent separation of the dilatometer parts, springs were attached to hooks on the sides of the cup and capillary.

The specific volume of each polymer was first measured at 25° in a calibrated pycnometer with water as the confining fluid. From the changes in the height of the mercury in the dilatometer, it was then possible to calculate the specific volumes of a polymer, after corrections were made for the expansion of the mercury and the Pyrex dilatometer.

The specific volume *versus* temperature plots are S-shaped curves, characteristic of first-order transitions. Figures 1 to 3 are typical of these curves, and Table II summarizes the information obtained from the experimental data.

In this table the percentage and the actual specific volume changes on melting are noted for each polymer. The "melting range" is defined here as that temperature interval over which the middle three quarters of the volume change occurs when the polymer is melted, and the "melting

TABLE III

X-RAY DATA

Polymer	Spacing d/n, Å.	Intensity
Wide angles		
Octadecyl methacrylate	4.18	S[a]
Hexadecyl methacrylate	4.16	S
Hexadecyl acrylate	4.16	S
	7.7	Grainy line
Small angles		
Octadecyl methacrylate	30.8	D[b]
Hexadecyl methacrylate	16.3	D
	51.1	D
	120	D
	110	D
Hexadecyl acrylate	139	D
	110	D

[a] S = strong. [b] D = diffuse.

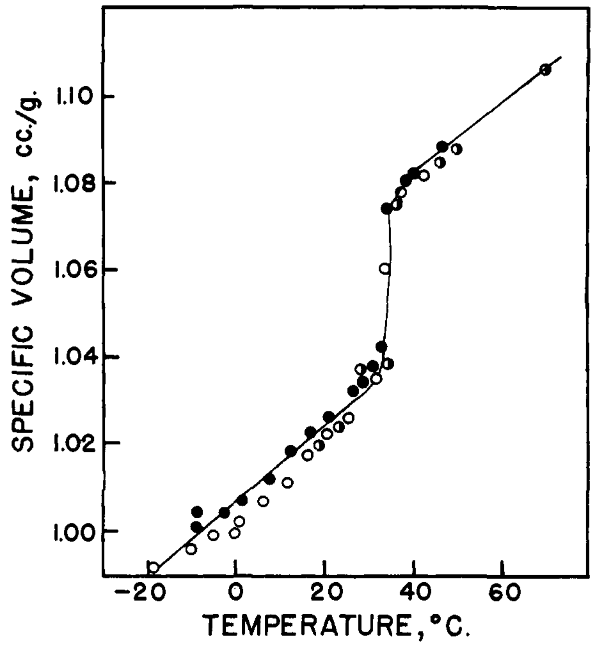

Fig. 1.—The melting curves of polyoctadecyl methacrylate crystallized at (○) −30°, (●) −10° and (◐) 10°.

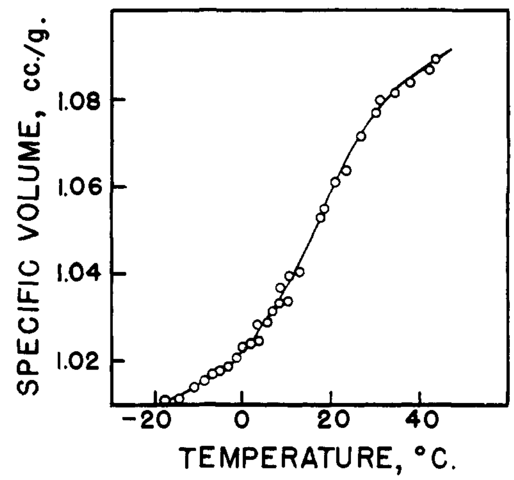

Fig. 2.—The melting curve of the equimolar copolymer of octadecyl and tetradecyl methacrylate.

point" is arbitrarily taken as the point of steepest slope in the specific volume *versus* temperature curve. Rates of crystallization were determined by measuring the changes in specific volumes of the polymers at some constant temperature after the polymers had been melted at 70°.

X-Ray Measurement.—An attempt was made to study the structure of the crystallites in these polymers by X-ray techniques. Short spacings were measured on Debye–Scherrer patterns taken with a cylindrical Philips camera of 57.3 mm. radius. Small angle patterns were made at a 20-cm. specimen-to-film distance with nickel-filtered copper radiation in an effort to obtain the wide spacings. A few polymers were drawn in an attempt to orient the crystallites, and patterns of these polymers were taken at a 4-cm. specimen-to-film distance. In Table III a summary of the results is presented.

Results and Conclusions

The Rates of Crystallization.—Of all the polymers examined, the crystallization of polyoctadecyl methacrylate (expt. 1) was most thoroughly studied. The rates of crystallization of the polymer were measured in −30, −10, 1 and 10° constant temperature baths. In each case, the crystallization was so rapid that the specific volume did not change after thermal equilibrium had been established (about 5 minutes).

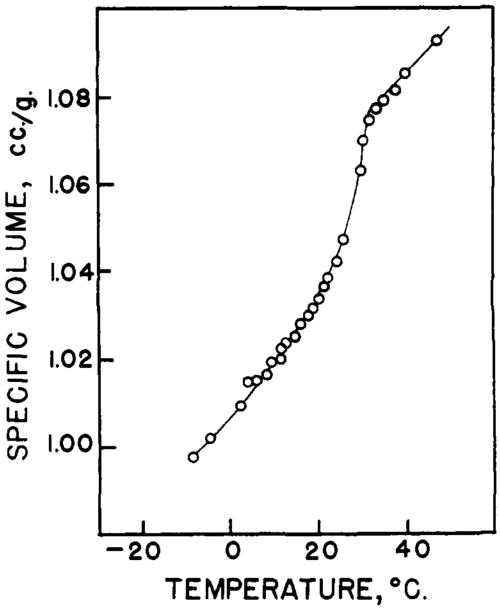

Fig. 3.—The melting curve of the copolymer of octadecyl (69.5%) and methyl (30.5%) methacrylate.

The same rapid rate of crystallization was observed in all the other polymers except polytetradecyl methacrylate which reached a specific volume equilibrium at −30° in about 20 minutes. When polymers were placed in baths well below the melting point, no supercooling was noted. However, supercooling was sometimes observed when polymers were slowly cooled from temperatures above the melting points. Thus, in several cases heating and cooling curves showed slight hysteresis effects.

The crystallization behavior of the polymers is probably due to the ease of crystallization of the symmetrical side chains which make up the major portion of the polymers. A similar rapid rate of crystallization and small amount of supercooling have been found in polyethylene.[11]

The Effect of the Temperature of Cooling on the Melting Range.—Melting curves were obtained for polyoctadecyl methacrylate cooled at the temperatures described in the previous section. Figure 1 shows graphically that the temperature of the cooling bath has no appreciable effect on the melting range which does not extend over 2° in length. Therefore, in this behavior also these polymers differ from natural rubber,[8a] the melting range of which is a function of the temperature of crystallization.

Melting Ranges of Polymers.—The sharpness of the melting ranges of the methacrylate and acrylate polymers is clearly indicated in Table II and in Fig. 1. It may be seen that the ranges do not exceed 5°, and that the average length is 3°.

The melting points listed in Table II follow

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(11) W. O. Baker and C. S. Fuller, *Ind. Eng. Chem.*, **38**, 272 (1946).

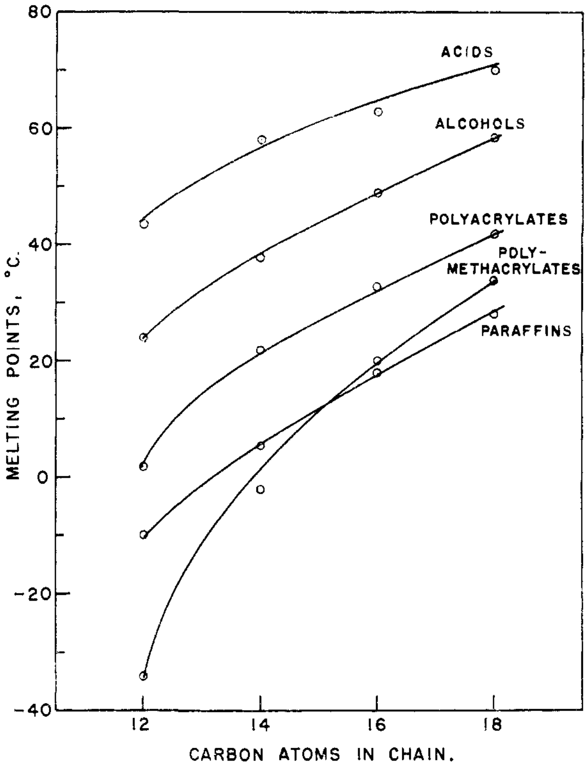

Fig. 4.—Melting points as a function of the length of the *n*-alkyl chain.

closely the brittle points of Rehberg and Fisher.[4] It is thus possible to go from a crystalline, wax-like solid to a viscoelastic material at the melting points of these solids.

Melting Ranges of Mixed Long Chain Copolymers.—It is assumed in this study that the composition of a copolymer is the same as the reaction mixture from which it was prepared because the reactivity of the monomers would not be expected to change appreciably with the length of the *n*-alkyl group. The mixed long chain copolymers (expts. 7, 8, 20) show interesting melting curves and ranges entirely different from those of the pure polymers. For example, the melting range of the equimolar copolymer of octadecyl and tetradecyl methacrylate (Fig. 2) extends between the melting points of the pure polymers. In this case the melting range extends from 6 to 26°, which is between the melting points of −2° for tetradecyl methacrylate and 34° for octadecyl methacrylate. The 18° melting point of this copolymer is almost midway between the melting points of the polymers of tetradecyl and octadecyl methacrylate. The range of the copolymer of octadecyl and hexadecyl methacrylate extends from 14 to 24° with a melting point of 22°.

In a like manner polydodecyl methacrylate prepared from a commercial mixture of monomers has an intermediate melting point of −16° and a melting range of 9°. It would seem reasonable to assume that the side chains are isomorphic and form solid solutions.

The Melting Behavior of the Copolymers of the Long Chain Monomers with their Methyl Analogs.—In general, the melting points of the long chain polymers are not markedly affected by the introduction of methyl analogs into the polymeric chains (Table II). However, the copolymers of octadecyl and methyl methacrylate (expts. 18, 19, 21, 22) show (except for the 59.5–40.5% copolymer) a decrease in the specific volume change on melting with the increase in the methyl monomer content until with 63 mole % methyl monomer in the copolymer no melting curve is found. This increase in amorphous structure with methyl monomer concentration is also seen in the X-ray patterns of the copolymers.

It may also be noted in Table II that the melting ranges of the methacrylate and acrylate copolymers are broader than those of the long side chain polymers.

Since the major portion by weight of the copolymers is in the long side chains which make up the crystallites, it is not surprising that the locations of the melting ranges are not markedly affected by the introduction of methyl groups. However, the mechanical behavior of the copolymers changes markedly with increase in the concentration of the methyl monomer, because of the larger fraction of amorphous material.

Specific Volume Changes on Melting.—The percentage and actual specific volume changes were estimated from the melting curves of the polymers and copolymers and the values are listed in Table II. Differences in these values for any pair of similar polymers (expts. 12 and 1, 14 and 2) are probably due to variations in the experimental conditions under which each was prepared. However, for any particular polymer the measurements (Fig. 1) are reproducible within experimental error.

Singleton and Gros[12] have shown that the molar specific volume changes of the C_{12} to C_{18} even-numbered, *n*-alkyl acids and their glyceride esters are proportional to the amount of straight chain hydrocarbon in the compounds. A rough estimate was made of the amount of crystallinity in the side chain polymers by assuming that the molar specific volume changes on melting in the polymers are the same as those for the acids. Calculations of this type indicated that the following percentage of the hydrocarbon chains crystallized: polyoctadecyl methacrylate, 25%; polyhexadecyl methacrylate, 19%; polytetradecyl methacrylate, 13%; polydodecyl methacrylate, 16%; polyoctadecyl acrylate, 38%; polyhexadecyl acrylate, 47%; polytetradecyl acrylate, 30%; and polydodecyl acrylate, 12%. The specific volume changes of the mixed long chain copolymers and the copolymers with less than 35% methyl monomer indicate that these materials have crystallized in an amount similar to that of the polymers.

X-Ray Diffraction.—The X-ray results indicate that the polymers and copolymers of the higher *n*-alkyl methacrylates and acrylates are crystalline and that the crystallites are made up of segments of the side chains. Reproducible spacings at approximately 4.2 Å. are found in the polymers. Similar spacings are also found in octodecyl, hexadecyl and tetradecyl alcohols, paraffin, hexadecanoic acid and aluminum stearate. The longer

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(12) W. S. Singleton and A. T. Gros, *J. Am. Oil Chem. Soc.*, **29**, 149 (1952).

spacings were, however, not reproducible and did not show any ordered pattern.

Orientation of the crystallites was not accomplished by stretching the melted polymers. It is obvious that additional study is necessary in order to understand more completely the structure and arangement of the crystallites.

Melting Points as a Function of the Length of the Straight Side Chains.[13–17]—The melting points of the even-numbered *n*-alkyl chain (12 to 18 carbon atoms) alcohols,[18] acids,[18,19] paraffins,[14] polymethacrylates and polyacrylates are plotted in Fig. 4 as a function of the number of carbon atoms in the chain. It may be noted in Fig. 4 that the curves (except for the polymethacrylates) are essentially similar in shape.

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[13] H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York, N. Y., 1950.

[14] M. D. Tilicheev, V. P. Peshkov and S. A. Yuganova, *Zhur. Obshcheĭ Khim.*, **21**, 1229 (1951).

[15] W. Sakai and T. Seiyama, *Busseiron Kenkyû*, No. 28, 29 (1950).

[16] W. E. Garner, K. Van Bibber and A. M. King, *J. Chem. Soc.*, 1533 (1931).

[17] W. E. Garner, F. C. Madden and J. E. Rushbrooke, *ibid.*, 2491 (1926).

[18] L. F. Fieser and M. Fieser, "Organic Chemistry," D. H. Heath and Co., Boston, Mass., 1944.

[19] T. L. Ward and W. S. Singleton, *J. Phys. Chem.*, **56**, 696 (1952).

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Structures and π-Electron Spectra. II. The Transformation Matrix[1,2]

BY WILLIAM T. SIMPSON AND CATHERINE WORSFOLD LOONEY

RECEIVED JUNE 18, 1954

A definite procedure is presented for the construction of a transformation matrix which relates π-electron spectra to structures. Arbitrariness in the transformation matrix which may exist even after the incorporation of symmetry is discussed. A method of removing the arbitrariness is shown, as applied to crystal violet and *p*-methoxy malachite green.

Introduction

In a previous paper,[3] hereafter called paper I, a scheme for using structures as an aid in understanding π-electron spectra was presented. The scheme usually requires the solution of a preliminary problem, preliminary in the sense that its solution does not lead directly to theoretical predictions but only "paves the way." The preliminary problem is to transform suitably to non-diagonal form a given observed set of term values arranged along the diagonal of a square matrix. The matrix before transformation is considered to be the dynamic variable electronic energy in the Heisenberg representation.

The actual method of computing the transformation matrix for forming a new non-diagonal matrix of the energy was not given in paper I (though an example of the procedure to be followed was given in Appendix I). In the present paper the object is to define a particular representation in which the energy is non-diagonal, and which is called the structure representation; and to show how to construct the transformation matrix. The transformation matrix is not always unambiguously determined, and the ambiguity is given detailed treatment. A particular method of removing the ambiguity is described, using as examples a given molecule (crystal violet) and another (*p*-methoxy malachite green) which is considered as a perturbation. This choice of examples is also a preparation for paper III of this series, which deals at length with triphenylmethane dyes, and which will illustrate the making of predictions using the scheme in paper I. We now give a formal statement of the object of this paper.

Given a diagonal energy matrix **E** the problem is to find the transformation matrix **S** such that

$$\mathbf{E}' = \mathbf{S}^{-1}\mathbf{E}\mathbf{S}$$

where **E′** is in the structure representation, a representation defined by the requirement that the matrix elements be labeled with indices which correspond to structures. Unit vectors in this representation refer to the same quantum states (not stationary states) as described by wave functions which correspond to structures, in that the squares of the wave functions transform like the corresponding structures.

Applying the methods of part I of paper I we consider as given (i) *n* structures and their behavior under the operations of the group of the molecule; (ii) *n* energy levels (the observed spectroscopic term values which are the elements of the diagonal matrix **E**) and their species. In addition we know that (iii) the transformation properties of the structures are consistent with the species of the states of the molecule.

Preliminary Discussion.—In this section we shall discuss qualitatively how the transformation matrix is to be calculated, but first shall present the notation that is to be used subsequently. The species of the levels are arranged serially in the order of the diagonal elements of **E**. There are *n* elements

$$E_{11}, E_{22}, E_{33}, \ldots, E_{nn}$$

with species[4]

$$\Gamma_\alpha, \Gamma_\beta, \Gamma_\gamma, \ldots, \Gamma_\nu$$

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[1] Presented in part at the Spectroscopy Symposium, Ohio State University, Columbus, Ohio, June 1953.

[2] Supported under Contract R-351-20-2 Air Research and Development Command.

[3] W. T. Simpson, THIS JOURNAL, **75**, 597 (1953).

[4] This notation is used in preference to $\Gamma_1, \Gamma_2, \Gamma_3, \ldots, \Gamma_n$ because conventionally Γ with a numerical subscript stands for a particular species, instead of one of serially numbered species for a particular dynamical system.