

Characterization of Block and Random Ethylene-Propylene Copolymers by Differential Thermal Analysis*

EDWARD M. BARRALL II, ROGER S. PORTER, and JULIAN F.
JOHNSON, *Chevron Research Company, Richmond, California*

Synopsis

A group of C^{14} -tagged ethylene and propylene polymers consisting of physical mixtures of homopolymers, block copolymers made up of two homopolymer sequences, and block copolymers made up of several homopolymer segments has been studied by differential thermal analysis (DTA). The effect of randomness in copolymers has also been studied in this set of systems, which contains 0-51 wt.-% ethylene. Block copolymers and physical mixtures have been found to have thermograms with endothermal minima at approximately 138 and 163°C. The ratio of heights of the two minima has been found to be a function of the ethylene and propylene content for mixtures of homopolymers and for block copolymers without randomness. DTA thus provides an analysis for monomer ratios in physical mixtures and in block copolymers of ethylene and propylene. The cooling thermograms of block copolymers have been demonstrated to have two exotherms in all cases where the block ethylene content exceeded 10%; the propylene limit was not fixed. Mixed homopolymers do not exhibit two freezing exotherms. The total heat of fusion of the polymer has been found to be a usable measure of chain randomness and block nature. The conditions for observation of single and multiple transitions have been extended.

The techniques of DTA have been applied to the field of polymer analysis in the past by a number of workers. Recently, Clampitt¹ has studied the thermal behavior of mixtures of high- and low-density polyethylene and used the DTA endotherms to estimate relative concentrations of the two similar polyolefins. The technique proved satisfactory in cases where corresponding crystalline states could be obtained and reproduced.

Ke has pointed out that block poly(ethylene-propylene) copolymers have two endothermal transitions as determined by DTA which are separated by approximately 30°C.² The first transition corresponds to the melting of polyethylene blocks at 130°C. and the second to the melting of polypropylene blocks at 162°C., according to Ke's observations.³ Ke also noted that the same two endotherms were obtained when intimate physical mixtures of the two homopolymers were thermographed. Cooling curves from block copolymer and homopolymer systems, however, did show significant

* Presented in part before the Division of Polymer Chemistry, 148th National Meeting of the American Chemical Society, Chicago, August 30-September 4, 1964.

differences between the true block copolymer system and a simple physical mixture.² Mixed homopolymers showed a single exotherm, as also reported by Inoue,⁴ while cooled block copolymer showed two exotherms at 158 and 119°C. The cooling exotherms have been explained by proposing that the propylene segments in the copolymer recrystallize sharply near the normal melting point of polypropylene, whereas the homopolymer propylene is subject to a 40°C. supercooling. This supercooling of polypropylene has been noted by other workers.³

The effect of the ethylene content, the block length, and degree of randomness on the thermogram of poly(ethylene-propylene) has not been reported previously and is the subject of this work.

EXPERIMENTAL

Results are developed on polymers with varying degrees of random and block copolymer sequencing of ethylene and propylene. Briefly, the synthesis proceeded as follows. Known amounts of monomer, some C¹⁴-tagged, were polymerized by an Al(C₂H₅)₂Cl plus TiCl₃ catalyst in purified heptane. A random copolymer containing some homopolymer was also prepared by using the nonstereospecific catalyst, aluminum alkyl plus VOCl₃. Polymerizations were performed under nitrogen at 70°C. in Fischer-Porter bottles. Polymer product was diluted with excess isopropanol containing HCl. Polymer was recovered by filtration followed by a methanol wash and final drying in a vacuum oven at 115°C. Various types of polymer; block copolymer with two homopolymer segments (bisegment blocks), block copolymer with several homopolymer segments (multisegment blocks), random copolymers, and intimate physical mixtures (molecular mixtures) of whole polymers, were prepared by variously mixing monomers beforehand and/or by degassing and purging between additions of different monomer. Physical mixtures were also made by intimately blending weighted amounts of the homopolymer powders. Some of the block copolymers were made without complete degassing between ethylene and propylene feeds. This produced polymers which were assumed to have, on the basis of synthesis, random polymer links between homopolymer ethylene and propylene blocks.

Compositions are qualitatively determined by monomer stoichiometry. Analyses were also developed by other techniques such as radioactive measurement of β -emission of C¹⁴ incorporated in the original monomers. Carbon-14 was counted by burning the samples in a microcombustion furnace followed by absorption of CO₂ in methanol and counting in a toluene-phosphor solution. Specific activity was determined by radioassay of homopolymers prepared from C¹⁴-tagged monomer. Table I shows the radiocarbon analyses. The radiometric method gives a direct and absolute measure of ethylene content which is independent of secondary factors.

Prior to analysis by DTA, each sample was heated to 160°C. in a nitrogen atmosphere and cooled at the rate of 0.5°C./min. This standardized annealing process permitted each material to approach maximum crystallinity

TABLE I
Analytical Data for Physical Mixtures and Ethylene-Propylene
Block Copolymers

Sample	Ethylene, wt.-% ^a	Peak Height Ratio	Type of sample	Freezing Curve Exotherms, °C.
3-14	0.0	0.	Homopolymer propylene	103
3-2	3.0 ± 0.5	0.172	Multisegment block	102
3-3	7 ± 1	0.206	Multisegment block	102
3-6	18 ± 1	0.325	Multisegment block	140, 111
3-13	49 ± 2	0.675	Multisegment block	140, 110
3-30	6.0 ± 0.2	0.125	Multisegment block with randomness	100
3-31	9.1 ± 0.2	0.170	Multisegment block with randomness	100
3-32	14.9 ± 0.3	0.376	Multisegment block with randomness	139, 110
3-40	18.1 ± 0.5	0.315	Bisegment block	141, 111
3-41	18.6 ± 0.4	0.328	Molecular mixture ^b	100
3-33	23.3 ± 0.1	0.410	Multisegment block with randomness	140, 110
3-35	25.3 ± 0.2	0.390	Bisegment block	140, 110
3-34	36.0 ± 0.4	0.570	Multisegment block with randomness	140, 110
1	9.35	0.217	Physical mixture of homopolymers	110
2	5.0	0.147		110
3	26.0	0.406		110
4	49.0	0.672		110
5	17.0	0.308		110
6	5.0	0.150		110
7	9.0	0.238		110
8	34.0	0.512		110
9	100.	0.	Homopolymer ethylene	113

^a Radiometric analysis. Physical mixtures were made up by weight from 100-mesh polymer flour.

^b Made by polymerizing ethylene in the presence of finely divided polypropylene.

and offered an excellent reference history for making comparisons between polymers.

The differential thermograms were obtained by using the adiabatic DTA equipment described previously.^{5,6} The polymer sample, about 10 mg., was weighed onto a 1-cm. square sheet of aluminum foil. The foil was carefully folded into a small packet and placed in the sample cup of the DTA apparatus. For the measurements requiring only the determination of peak height, a heating rate of 8°C./min. was employed. For calorimetric determinations, heating rates of 1, 2, 4, 8, and 10°C./min. were used. Peak heights were determined with a vernier rule from the base line, drawn as shown in Figure 1. The sum of the peak heights divided into the height of

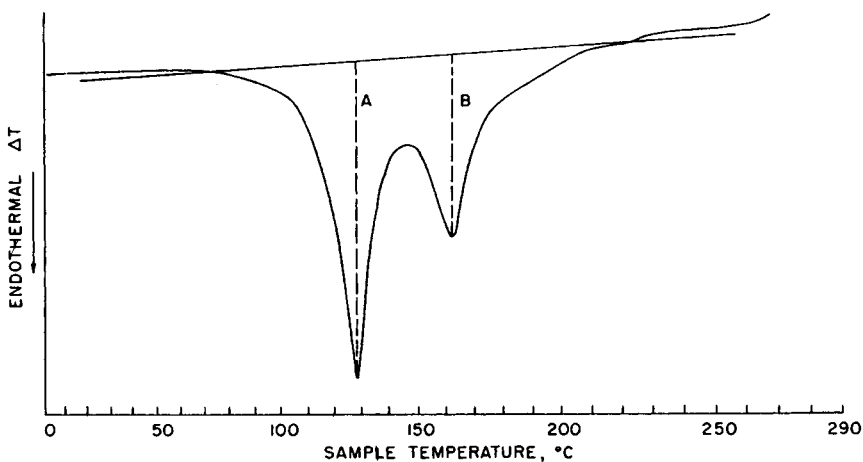


Fig. 1. Differential thermogram of 51% ethylene-49% propylene block copolymer: (A) ethylene peak height; (B) propylene peak height; 0.0098-g. sample heated at 8.7°C./min.; $\Delta T = 8.0$ mv./in.

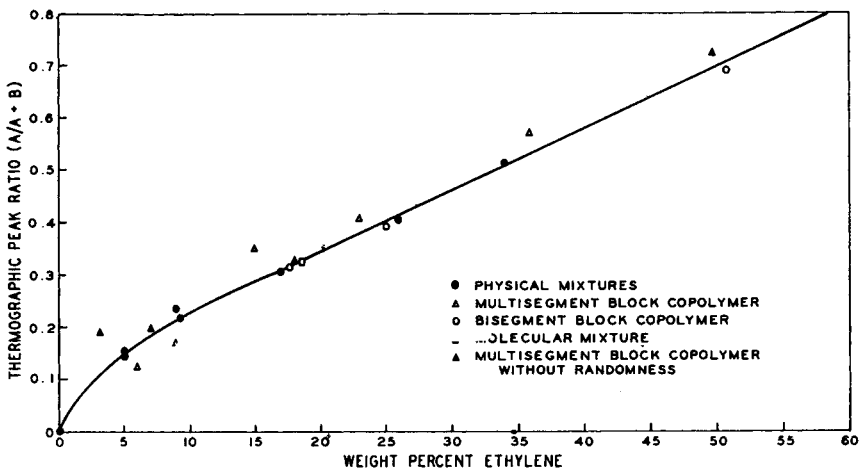


Fig. 2. DTA studies of ethylene-propylene polymers.

the polyethylene endotherm represents the peak height ratio shown in Figure 2. The peak height ratios for nine samples of copolymer and seven samples of homogeneous mixtures of the pure homopolymers are shown in Figure 2 graphed versus the radiometric ethylene analyses.

Cooling curves were carried out by programming downward at 8°C./min. The downward program was accomplished by reversing the programmer motor and opposing the heater with a baffled jet of carbon dioxide. This resulted in a linear downward program which was accurate and smooth to within 2°C. in 100°C. The carbon dioxide jet was shielded so that no channeling of the gas in one part of the apparatus was noted.

RESULTS

Block and Random Copolymers

A representative differential thermogram of a block copolymer is shown in Figure 1. Two endothermal minima are shown located at 128 and 163°C. This is in good agreement with previously published data.²

The thermogram of a random copolymer made from a mixture of ethylene and propylene gases polymerized in the presence of a nonstereospecific catalyst, aluminum alkyl plus vanadium oxychloride, shows no endothermal minima. The crystallinity of this material may be assumed to be near zero, and no thermal absorption can be expected.

A random copolymer (containing traces of homopolymer) formed from mixed ethylene and propylene gases polymerized in the presence of a stereospecific catalyst, titanium trichloride and diethyl aluminum chloride, exhibits some thermal absorption (Fig. 3). Endotherms are observed at 98 and 123°C. The heat of fusion of a 49% ethylene copolymer was 16 cal./g., as calculated from the area including the 98°C. shoulder and the 123°C. minima. The ratio of the shoulder to the minima was not directly related to the ethylene content, as shown with block copolymers according to calibration curves. Due to the overlap which occurs between the endotherm of block copolymer ethylene (129°C.) and the random copolymer (123°C.), the shift in the endothermal minimum temperature is not a reliable indication of the random copolymer content.

Peak Height Ratio and Composition

The ratio of polyethylene to polypropylene in a simple physical mixture of the homopolymers is consistently reflected in the ratio of their respective fusion endotherms obtained by DTA. This is amply demonstrated in Figure 2. It is important to note that no serious departure from this peak

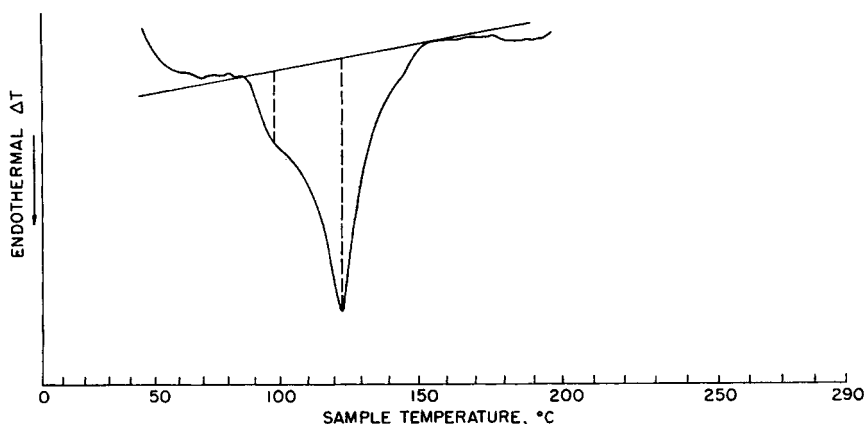


Fig. 3. Differential thermogram of 49% ethylene-51% propylene in a random copolymer, stereospecific catalyst; 0.0156-g. sample heated at 8.7°C./min.; $\Delta T = 4$ mv./in.

height relationship with ethylene content is seen among samples of bisegment block ethylene-propylene copolymers, homopolymer mixtures, and multisegment block copolymers so long as the conditions of synthesis were adjusted so that there is little or no randomness between blocks.

The bend in the curve shown in Figure 2 is due to a characteristic of peak height measurement in DTA, not necessarily to some function of the polymer systems. Barrall and Rogers⁷ noted the same dependence when the peak height of salicylic acid fusion endotherm was plotted versus the salicylic acid content in carborundum mixtures. In the polymer and salicylic acid cases, the composition curve is linear above 6% of the active material causing the endotherm measured. Inoue suggests that the apparent degree of crystallization in mixtures is greater for the major component than for the minor.⁴ The crystallinity ratio can also vary with polymer ratio.

Multisegment block copolymers with random sequences do not fit the previously established relationship between peak height ratio and ethylene content. The peak height ratios above 10% ethylene are too large for the indicated ethylene content as determined by the radiometric method. Below 10% the ethylene heights are too small. This variation can be explained on the basis of previous DTA on random copolymers. Where the degree of crystallinity is very low, as in the case of the copolymer made from mixed gases over a nonstereospecific catalyst, no thermogram is obtained. In that case, any tagged ethylene present in a truly random sequence does not crystallize and will not be observed by DTA. Therefore, the peak height ratio of the block copolymer containing these random sequences will be smaller than that expected from the radiometric data and the relationship shown on Figure 2.

Experimental data on two multisegment block copolymers containing less than 10% ethylene bear out the low ratio conclusion. Above 10% the peak ratios are too large. This can be accounted for by examining the thermogram of the random copolymer made with a stereospecific catalyst (Fig. 3). The whole endotherm of this polymer lies within the temperature region for the endotherm due to the polyethylene block. Therefore, in the measurement of peak height ratio with the crystalline random polymer adding only to the ethylene endotherm, a high number will be obtained. Indeed, Jackson has shown that there is no evidence of polypropylene crystallinity in partially crystalline ethylene-propylene copolymers with $\geq 60\%$ ethylene prepared with Ziegler-Natta catalyst.⁸ The effects of chain randomness are further supported by pyrolysis-gas chromatographic results, to be reported elsewhere.

Heat of Fusion and Copolymer Structure

Heats of fusion were obtained from planimeter integration of differential thermograms run at several heating rates by the method described previously.⁵ The thermograph was calibrated for calorimetry by determining the areas at several heating rates for the endotherms caused by the solid-solid transitions of NH_4Br and NH_4Cl and the solid-liquid transition of benzoic acid.

The calorimetric values independently measured here for ethylene and propylene homopolymers (Table II) lie within the limits established by Inoue.⁹ The higher heat and entropy of fusion of polyethylene over polypropylene is confirmed. Bisegment polymers show heats of fusion almost equivalent to those of the physical mixtures, i.e., very close to the values calculated from homopolymer percentages. The multisegment block copolymers with randomness show heats of fusion 6–10 cal./g. lower than corresponding physical mixtures. Simple multisegment copolymers without randomness have heats of fusion comparable to bisegment and physical mixtures. The wider variation in multisegment block copolymers is due, presumably, to some randomness in the chain between blocks in certain samples. All of these effects are in accord with the degree of crystallinity expected from the various methods of copolymer synthesis.

TABLE II
Heats of Fusion for Block Copolymers and
Physical Mixtures of Polyethylene and Polypropylene

Sample	Ethylene, wt.-%	Type of sample	ΔH_f , cal./g.	
			Found	Calculated ^a
3-14	0.0	Homopolymer propylene	13.1	—
3-2	3.0 ± 0.5	Multisegment block	12.2	14.4
3-3	7 ± 1	Multisegment block	14.8	16.2
3-6	18 ± 1	Multisegment block	17.3	21.1
3-13	49 ± 2	Multisegment block	31.0	35.1
3-30	6.0 ± 0.2	Multisegment block with randomness	11.3	15.8
3-31	9.1 ± 0.2	Multisegment block with randomness	14.0	17.3
3-32	14.9 ± 0.3	Multisegment block with randomness	9.0	19.9
3-40	18.1 ± 0.5	Bisegment block	20.1	21.0
3-41	18.6 ± 0.4	Molecular mixture	21.3	21.5
3-33	23.3 ± 0.1	Multisegment block with randomness	19.2	23.6
3-35	25.3 ± 0.2	Bisegment block	23.7	24.5
3-34	36.0 ± 0.4	Multisegment block with randomness	23.0	29.3
1	9.35	Physical mixtures of homopolymers	16.6	17.3
2	5.0		16.0	15.4
3	26.0		23.9	24.8
4	49.0		33.9	35.1
5	17.0		20.1	20.8
6	5.0		16.0	15.4
7	9.0		17.9	17.3
8	34.0		27.3	28.4
9	100.		58.1	—

^a Calculated from the ΔH_f of polyethylene (58.1 cal./g.) and polypropylene (13.1 cal./g.) used in this study without attempting to account for crystallinity,

Crystallization Exotherms

Ke has previously reported two freezing exotherms for block copolymers and only one exotherm for physical mixtures.^{2,3} The block copolymers, both bisegment and multisegment, studied here showed this behavior when the ethylene block content was above 10%. Below 10% ethylene only one freezing exotherm was noted. It was not possible to fix the lower limit for propylene content for one exotherm with available samples. The lack of two freezing points is due to the short length of the ethylene segments which are apparently unable to influence the polypropylene supercooling.

CONCLUSIONS

DTA furnishes a reliable method for the analysis of physical mixtures and for multisegment and bisegment block copolymers of ethylene and propylene in cases where chain randomness is minor. If a secondary method of analysis which is independent of crystallinity is possible, e.g., use of tagged samples, the DTA method can aid in elucidating the chain structure, including degree of copolymer randomness. The peak height ratio coupled with the heat of fusion alone represents a rough measure of the degree of block randomness.

The following conclusions can be drawn from Tables I and II. Multisegment block copolymers are characterized by heats of fusion almost equal to or lower than corresponding physical mixtures. Bisegment block copolymers have heats of fusion equivalent to physical mixtures within experimental error. Cooling curves definitely indicate that samples 3-6 and 3-13 are block copolymers according to Ke's criterion of double exotherms. Sample 3-3 may be inferred to have a large amount of randomness between blocks from its low heat of fusion, which is comparable to that of polymers with known randomness.

Samples 3-35 and 3-40 are both block copolymers by the double freezing point technique. The block copolymer identification and the high heat of fusion (almost as large as a comparable physical mixture) indicate long block length and only a few blocks. Very little randomness is present (compare data of Fig. 2).

Low heats of fusion consistent with short block segments in sequential arrangement are noted for samples 3-30 and 3-31. No confirmation of the block nature can be obtained from freezing point data due to low ethylene content. The displacement from curve in Figure 2 indicates noncrystalline segments in the chain.

Multisegment block copolymers are identified from heat of fusion data and freezing point thermograms; note samples 3-32, 3-33, and 3-34. The location of the peak height ratios in Figure 2 indicates the presence of random copolymer with some crystallinity between blocks in all cases.

References

1. Clampitt, B. H., *Anal. Chem.*, **35**, 577 (1963).
2. Ke, B., *J. Polymer Sci.*, **42**, 15 (1960); *ibid.*, **61**, 47 (1962).
3. Ke, B., *Organic Analysis*, Vol. 4, J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger, Eds.; Interscience, New York, 1960.
4. Inoue, M., *J. Polymer Sci.*, **A1**, 3427 (1963).
5. Barrall, E. M., II, J. F. Gernert, R. S. Porter, and J. F. Johnson, *Anal. Chem.*, **35**, 1837 (1963).
6. Barrall, E. M., II, R. S. Porter, and J. F. Johnson, *Anal. Chem.*, **36**, 2172 (1964).
7. Barrall, E. M., II, and L. B. Rogers, *Anal. Chem.*, **34**, 1106 (1962).
8. Jackson, J. F., *J. Polymer Sci.*, **A1**, 2119 (1963).
9. Inoue, M., *J. Polymer Sci.*, **A1**, 2697 (1963).

Résumé

On a étudié par analyse thermique différentielle (ATD) tout un groupe de polymères de l'éthylène et de propylène marqués au C¹⁴ et constitués de mélanges physiques d'homopolymères, de copolymères en blocs formés de deux séquences homopolymériques, et de copolymères en blocs formés de plusieurs segments homopolymériques. L'influence du caractère statistique des copolymères a aussi été étudiée dans ce groupe de systèmes, lequel contient de 0 à 51% en poids d'éthylène. On a trouvé que les copolymères en bloc et les mélanges physiques avaient des thermogrammes avec des minima endothermiques aux environs de 138 et de 163°C. On a trouvé que le rapport des hauteurs des deux minima est une fonction de la teneur en éthylène et en propylène. Pour les mélanges d'homopolymères et pour les copolymères en bloc sans variation statistique. L'ATD fournit donc une analyse des rapports entre monomères dans les mélanges physiques et dans les copolymères en bloc d'éthylène et de propylène. On a démontré que les thermogrammes de refroidissement de copolymères en bloc ont deux isothermes dans tous les cas où la teneur en éthylène dans le bloc dépassait 10%; on n'a pas déterminé la limite en propylène. Les mélanges d'homopolymères ne montrent pas deux isothermes lors du refroidissement. On a trouvé que la chaleur totale de fusion du polymère est une mesure utilisable pour déterminer la structure statistique de la chaîne et la nature des blocs. On a étendu les conditions d'observation des transitions uniques et multiples.

Zusammenfassung

Eine Gruppe von C¹⁴-markierten Äthylen- und Propylenpolymeren, umfassend physikalische Mischungen von Homopolymeren, Blockcopolymeren mit zwei Homopolymersequenzen und Blockcopolymeren mit mehreren Homopolymersequenzen, wurde differentialthermoanalytisch (DTA) untersucht. Der Einfluss des Unordnungsgrades der Copolymeren wurde bei diesen Systemen, welche 0–51 Gewichts% Äthylen enthalten, ebenfalls untersucht. Blockcopolymeren und physikalische Mischungen lieferten Thermogramme mit endothermen Minima bei etwa 138 und 163°C. Das Verhältnis der Höhen der beiden Minima war bei Mischungen von Homopolymeren und bei geordneten Blockcopolymeren eine Funktion des Äthylen- und Propylengehalts. DTA ermöglicht so eine Analyse des Monomerverhältnisses in physikalischen Mischungen und Blockcopolymeren von Äthylen und Propylen. Das Abkühlungsthermogramm von Blockcopolymeren besaß in allen Fällen mit höherem Blockäthylengehalt als 10% zwei exotherme Maxima; für Propylen war kein Grenzwert vorhanden. Homopolymeregemische weisen keine zwei Gefrierexothermen auf. Die totale Schmelzwärme des Polymeren erwies sich als brauchbares Maß für die Ungeordnetheit der Ketten und für die Blocknatur. Die Bedingungen für die Beobachtung von einfachen und mehrfachen Umwandlungen wurden erweitert.

Received April 26, 1965