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THE THERMOGRAPHIC STUDY OF POLYMERS

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I. INTRODUCTION

Thermography[1] — an effective method of chemical study — was until recently comparatively little used in the study of polymers. In recent years, however, a large and increasing number of papers have been published on the use of thermographic methods in the chemistry of macromolecular compounds, and this makes it desirable to review this work and to describe the possibilities and future prospects of this method. The chapter in Ke's book on newer methods of polymer characterisation[2] contains interesting material, but does not exhaust the subject.

In the thermographic method, the change in the temperature of a specimen placed in a heating block is recorded as the latter is smoothly heated (or, less frequently, cooled). Particularly valuable information is obtained by recording the difference in the temperatures of the specimen being studied and a standard substance placed in the same block, or the difference in the temperatures of the specimen and the block itself. The resulting differential curve shows, in the form of peaks or other deviations from a straight line, all the thermal effects and all changes in thermal characteristics leading to more rapid or less rapid increase in the temperature of the specimen relative to that of the standard, within definite temperature ranges. This method is called differential thermal analysis (DTA). This term is being used increasingly as a synonym for thermography.

Usually, both the temperature of the specimen ("simple recording") and the above temperature difference are recorded simultaneously with respect to a time coordinate. At the present time, however, many papers give only differential curves.

Thermographic studies are carried out using photorecording instruments of different designs, for example, the Kurnakov apparatus[3] and its various modifications[4,5]. Recording on electronic potentiometers (recorders) is now widely used. The sensitive elements are usually low-inertia thermocouples, but resistance thermometers and thermistors are sometimes used. A general trend is the reduction of the size of the specimen from the previously used gramme quantities to milligrammes or fractions of a milligramme[6] without decrease in the sensitivity of the analysis and with the production of more highly resolved peaks.

Thermography is one of the basic methods for the phase analysis and thermal characterisation of substances. It also provides a means of studying various transformations taking place in substances, such as the aging of alloys[7]. Thermograms can be used for the quantitative estimation of thermal constants (heat capacity, thermal conductivity[8]), and to determine not only the temperatures but also the heats of phase transformations and chemical reactions: for a given heat transfer coefficient, the heat of the process is proportional to the area of the peak described by the differential curve during the corresponding transformation[9]. Although the theory of thermal analysis is still being developed[10], the thermographic method has provided the basis of a number of methods of determining thermal quantities — methods combined under the heading of thermographic calorimetry[11] — and also as a basis for the production of suitable apparatus[12].

A characteristic feature of the thermographic method is that in some cases different physical and chemical processes (for example fusion, boiling, and endothermic reactions) produce identical effects. It is therefore the task — sometimes not easy — of the research worker to interpret the thermograms obtained. For this purpose it is often necessary to carry out additional experiments in which the substance being studied is subjected to various forms of heat treatment, after which the thermogram is recorded again. The introduction of data obtained by other methods is also extremely useful.

While noting the fact that thermographic methods are comparatively little used in organic chemistry, Ravich[13] correctly points out that this situation has developed both as a result of certain scientific traditions, and also because of the specific features of the materials studied; he refers to the complicated structures of organic substances, and their ability to undergo supercooling, vitrification, the formation of a large number of non-equilibrium systems, etc. A rational explanation of the discrepancies in the data obtained by different workers who apparently studied identical materials can be obtained only by making allowance for the time factor[14]. These features are even more characteristic of polymers.

The applicability of thermographic methods to the study of polymeric materials is related to their tendency to undergo various physical and chemical thermal transformations. The various chemical processes — polymer formation, vulcanisation, thermal oxidation, and degradation — are accompanied by definite thermal effects. The conversion of a polymer from the vitreous state into the highly elastic state is accompanied by a change in the thermal characteristics. Crystallisation, fusion, and polymorphic transformations are accompanied by the liberation or absorption of heat. Fig. 1 gives a schematic thermogram[15] which covers the complete temperature range of existence of a polymer and illustrates the manifestation of most of the above processes. It is naturally a general scheme, to provide guidance in the study of specific thermograms†.

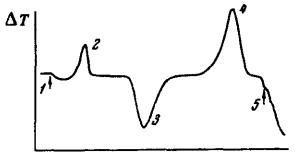


Fig. 1. Thermal processes in polymers (schematic):
1) vitrification; 2) crystallisation;
3) fusion; 4) oxidation; 5) degradation.

II. STUDY OF STRUCTURAL TRANSFORMATIONS

1. Thermographic Manifestations of Transformations in Homopolymers

In the study of polymers it is necessary to bear in mind the lack of correspondence between the structural and thermodynamic criteria of phase states[16]. X-Ray and crystal-optical methods give the structural characteristics of polymers, whereas thermographic methods give the phase characteristics.

Phase transformations characteristic of polymers include the formation of a crystalline phase from an amorphous phase (crystallisation) and the opposite process — fusion. For polymorphic crystalline polymers, interconversion of the modifications is also observed. The thermograms provide an objective representation of all these processes.

Vitrification. The conversion of vitreous polymers into a highly elastic or viscous-fluid state, and the opposite process, although they are essentially not phase transformations since they occur within a single amorphous phase, are accompanied by a change in a number of the properties of the polymers, including their thermal properties. As a result, despite the absence of the thermal effect characteristic of phase transformations, the thermogram shows a characteristic inflection: a change in the course of the differential curve from that characteristic of a polymer in the vitreous state to that characteristic of a polymer after softening. When the conditions of the experiment are unchanged, the magnitude of the inflection can be used to estimate approximately the quantity of amorphous phase in partly crystalline polymers.

Dudek and Lohr[17] used the thermographic method to study the vitrification temperature of poly(methyl methacrylate) and the influence of small quantities of monomer and plasticiser on this temperature. The vitrification of poly(methyl methacrylate) and atactic polypropylene was

† In all the Figures, as in most thermographic work, values of $\Delta T > 0$ (exothermic effects) are plotted upwards along the axis of ordinates, whereas values of $\Delta T < 0$ (endothermic effects) are plotted in the opposite direction. It should be borne in mind that a number of authors, chiefly foreign, use the opposite sign convention. Where their work has been used in the present review, the thermograms have been redrawn in accordance with the above principle.

studied by Strella [18], who proposed a method for calculating the heat capacity from the difference in the temperatures of the periphery and centre of a cylindrical specimen. This method was discussed and the calculation refined by Haly and Dole [19].

Wunderlich and Bodily [20] used "dynamic differential-thermal analysis", which makes it possible to compare a large number of thermograms recorded at different rates. They showed that for slowly annealed amorphous polystyrene the thermograms in the vitrification range show not simply the jump characteristic of the quenched specimen, but also a peak, which increases with the rate of heating. This method was also used to study the kinetics of the vitrification and softening of polystyrene [21]. Keavney and Eberlin [22], in a study of the vitrification of poly(vinyl chloride), polystyrene, etc., showed that change in the size of the specimen and the rate of heating has no significant influence on the transformation temperature T_g. Murphy [23] used a thermographic method to determine the dependence of the vitrification temperature on the molecular weight of polyacrylonitrile.

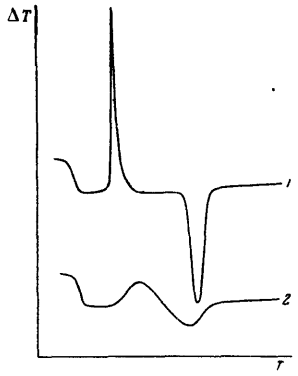


Fig. 2. Characteristic thermograms for an amorphous crystallising polymer: 1) with highly regular structure; 2) with lower regularity.

Crystallisation‡ can be observed on a thermogram if the rate of this process is commensurate with the rate at which the thermogram is recorded [25]. Since the thermogram usually covers an appreciable range of temperatures, the specimen during the experiment may find itself in a temperature range in which crystallisation takes place fairly rapidly; an exothermic effect will then appear on the thermogram. The absence of an effect from a given range does not indicate that crystallisation is not taking place. Thus the thermogram for amorphous natural rubber [26], which crystallises even at room temperature, does not show an exothermic effect in the corresponding range, since the process then takes place extremely slowly.

The intensity of crystallisation depends to a marked extent on the presence of crystalline nuclei in the bulk of the amorphous polymer [27]. Such nuclei may be provided, in particular, by traces of previously formed crystallites, which did not disappear completely when the polymer was converted into the amorphous state before the experiment. Sometimes, when the nuclei are removed completely, an exothermic effect may not appear on the thermogram, or the peak may be smaller and displaced towards higher temperatures.

Let us consider a polymer which is completely amorphous in the original state and which crystallises during the experiment (Fig. 2). The thermograms show a more or less sharp peak, whose area gives information on the integral heat liberation and hence on the total quantity of crystalline phase formed, and whose height gives information on the intensity of the process. A sharp high maximum indicates that all the material capable of crystallising has crystallised in a narrow time and temperature range ("explosively"). An equally sharp peak may be observed at a much higher temperature when the melt is cooled at the same rate. A broad range of intensive crystallisation is thus detected. The optimal temperature apparently lies in the middle of this range.

A high rate of crystallisation can be observed only in polymers with a highly regular structure. Decrease in regularity leads to a decrease in the rate of crystallisation, and the process then covers an appreciable temperature range. Considerable variations are observed in the degree of perfection or size of the resulting crystallites, and this is reflected in the considerable variation in their melting points. The temperatures of crystallisation and fusion of polymers differ considerably: definite melting points correspond to the observed temperatures of formation of crystallites [28]. This is also shown clearly on the thermograms. Illustrative data were obtained by Gray and Casey [29], who subjected polyethylene specimens, which had been converted into the amorphous form, to successive treatments at a series of decreasing temperatures. Each peak on the fusion thermogram corresponded to crystallites formed at a definite temperature (Fig. 3).

Fusion. In a thermographic experiment, crystallisation usually takes place at a continuously increasing temperature, and fusion also takes place continuously, over a wide temperature range. A flat exothermic crystallisation peak (curve *2* in Fig. 2) is often converted directly into an indistinct endothermic fusion minimum.

In many instances imperfect crystallites melt at temperatures favourable for subsequent crystallisation. Thus fusion is accompanied not only by formation of an amorphous phase but also by recrystallisation — the formation of more perfect crystallites melting at higher temperatures.

The dependence of the melting point on the rate of heating is due to two factors. The first of these — recrystallisation — tends to increase the temperature as the rate of heating is decreased, and is observed chiefly at low rates of heating. At rates of heating above a certain limit, the melting point is almost independent of the rate of heating [30] (it should be emphasised that here we are speaking not of

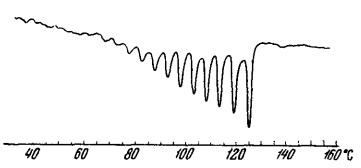


Fig. 3. Fusion of polyethylene crystallised at temperatures successively decreasing by 5 deg. [29]

‡ The crystallisation of polymers is discussed in detail in Mandelkern's monograph [24], but the thermographic method is not dealt with.

equilibrium fusion, but of metastable fusion). At high rates of heating, however, the second factor — superheating produced by kinetic factors — begins to operate in the opposite direction. It is here of interest to note the temperatures of three elements of the thermographic peak: the start, the peak value, and the end. For poly(tetrafluoroethylene)[31] at rates of heating reaching 46 deg min^{-1}, the superheating amounts to 30 deg, and is greater, the greater the molecular weight. The temperature of the start of fusion is independent of the rate of heating. At the intermediate rates used in thermographic studies, the possibility of superheating is small, and usually it is necessary to make allowance for the influence of only the first of the above factors.

The dependence of the temperature of the endothermic fusion peak T_{fusion} on the temperature at which crystallisation took place T_{cryst} (when almost no recrystallisation is observed during fusion) is close to linear (curve *1* in Fig. 4). The limiting melting point T_{lim} corresponding to the equilibrium crystals is characterised by the fact that the temperatures of crystallisation and fusion are equal. It can be found as the point of intersection of the extrapolated straight line giving the above relationship with a line drawn at an angle of 45° from the origin of coordinates ($T_{fusion} = T_{cryst}$). Using this method, Wyckoff[32] found the value 178.4° ± 0.3° for the limiting melting point of polypropylene. On recrystallisation, the curve giving the dependence of the melting point on the temperature of initial crystallisation undergoes a change in character; if the process took place under ideal favourable conditions, the crystallites formed at any temperature would reach the equilibrium state (line *2*). Usually, however, recrystallisation does not proceed to completion in a thermographic experiment, and the actual curve *3* lies between the two limiting straight lines.

Recrystallisation is revealed on the thermograms (Fig. 5) when the rate of this process is comparable to the rate of heating of the specimen during the thermographic experiment. Splitting of the fusion peak may be observed, due to superposition of the endothermic effect of fusion and the exothermic effect of crystallisation. By recording the thermograms at different rates, it is possible to observe a change in the ratios of the low-temperature and high-temperature peaks: the slower the rate of heating, the greater the relative magnitude of the latter. With very rapid heating, recrystallisation cannot take place at all. In this way it is possible to obtain proof that the splitting of the fusion effect is due to recrystallisation during the experiment. Frequently, however, the presence of two endothermic minima on polymer thermograms is due to other factors.

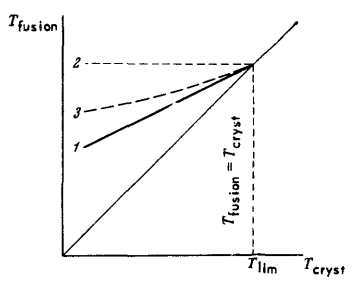


Fig. 4. Dependence of the melting point of a crystalline polymer on the temperature of crystallisation.

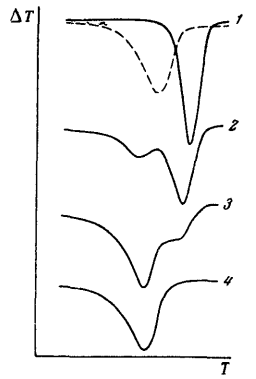


Fig. 5. Characteristic fusion thermograms for polymers in which the crystallites show a wide range of degrees of perfection. The rate of heating increases from 1 to 4; the broken line gives the hypothetical curve for where there is no recrystallisation.

Until now we have considered the thermograms of specimens in which the formation of crystalline phases takes place only during the actual thermographic experiment. Much more frequently, the crystallites in the specimens studied are formed at an earlier stage. The form of the thermogram then depends to a marked extent on the thermal pre-history of the material.

Since the crystallisation of a polymer can take place at a number of different temperatures, the crystallites obtained correspond to different endothermic peaks on the thermograms. For thermal analysis it makes no difference whether they correspond to different structural modifications (as for gutta-percha) or to crystallites of the same modification. This illustrates both the advantages and limitations of the thermographic method. On the one hand, it detects differences in super-molecular formations which cannot be detected even by X-ray diffraction. On the other hand, it cannot indicate whether the presence of two or more endothermic minima is due to differences in structure, recorded by X-ray diffraction, or to differences in the efficiency of aggregation. The existence of several endothermic effects with definite melting points (in the absence of polymorphic transformations) should not be regarded as an indication of the existence of the corresponding number of phases, since the crystallites of each type are not thermodynamically equivalent. Under favourable temperature conditions and over a sufficiently long period, they may all be converted into more stable crystallites with the "limiting" melting point. Thus the presence of these crystallites with different degrees of perfection, giving different peaks on the thermograms, is due not to thermodynamic but to kinetic factors.

Two or several fusion peaks are observed on a thermogram when the crystallisation has been carried out by treating the specimen at several gradually decreasing temperatures. On the other hand, when a specimen has been kept at several successively increasing temperatures, the thermogram shows only one endothermic peak, corresponding to the crystallites formed at the highest of the temperatures. (The previously formed low-temperature crystallites melt and undergo recrystallisation to different extents.)

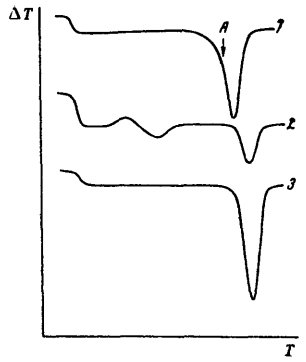


Fig. 6. Thermograms for crystalline polymers (schematic; see text for explanation).

If it can be assumed that the polymer has undergone recrystallisation, but that because of the relatively high rate of the thermographic experiment the process is revealed on the thermograms to only a very slight extent, it is best to treat the specimen in a special experiment for a more or less prolonged period at a temperature close to the melting point of the specimen, and then to verify, by repeating the recording, the efficiency of the recrystallisation process.

When non-equilibrium crystallites are heated for a relatively short period (at a temperature corresponding to point *A* on curve *1* in Fig. 6), only a small quantity of equilibrium phase is formed; the resulting amorphous phase is able to undergo only partial recrystallisation (the rate of crystallisation at this temperature is low), and can be detected in a subsequent experiment (curve *2* in Fig. 6): the thermograms show exothermic effects corresponding to the formation of new non-equilibrium crystallites from this amorphous phase, and the fusion of these crystallites. With increase in the duration of the constant-temperature treatment, the quantity of amorphous phase decreases and the quantity of equilibrium crystallites increases. The area of the peak and the peak temperature on the thermogram approach the limiting values (curve *3* in Fig. 6)[33].

Thus the thermographic method is extremely effective for the direct observation of the processes of crystallite formation and fusion in polymers, and also for phase analysis. It also reveals the thermal pre-history of a polymer specimen.

2. Thermographic Study of Individual Homopolymers

Early experimental results. The fusion and crystallisation of synthetic and natural polymers have been studied by a number of workers. Initially, the procedure used involved the construction of cooling and heating curves from data obtained by periodic temperature measurements (at isolated points). Baker and Fuller[34] and Jenckel and Wilsing[35] used this method to study crystallising polyurethanes and made a number of observations regarding the characteristic features of the fusion process, the dependence of the melting point on the conditions of crystallisation, etc.

The method of differential thermal analysis appears to have been used for the first time by Mikhailov and Klesman[36], who pointed out the characteristic features of the thermograms for two structural modifications of polyamides — crystalline and amorphous. They also undertook quantitative thermographic determinations of the heats of crystallisation and fusion of a polyamide of the polycaprolactam type. Even these early papers revealed the extensive possibilities provided by thermographic methods in the study of polymers, although the authors did not avoid a number of inaccuracies, in particular by attributing the endothermic effects to the conversion of the amorphous polymer from the vitreous state into the highly elastic state and from the highly elastic state into the viscous-fluid state. Subsequently, Mikhailov and Gorbacheva continued their studies of structural transformations in synthetic polyamides and polyesters[37], and studied the influence of the conditions of preparation, drawing, and heat treatment on poly(ethylene terephthalate) and fibres produced from it[38]. The same authors studied the influence of molecular weight (polycapramide and polypropylene), method of preparation — poly(vinyl alcohol) — and form (powder or fibre) (polyacrylonitrile) on the behaviour of polymers when heated[39]. Early work on the thermographic study of polymers includes Coste's work[40] on polyesters and polyamides.

Tolchinskii and coworkers[41] used the thermographic method to study polypropylene. They established the temperature limits of the crystallisation and fusion of the polymer, investigated the dependence of the crystallisation range on the rate of cooling, and estimated the degree of crystallinity of various polypropylene specimens.

Thermographic studies were also carried out by Ke, who examined various methodological features of the thermography of polymers and gave the differential-thermal heating and cooling curves for various grades of polyethylene, polypropylene, their mixtures[42], copolymers, and block-copolymers[43], and also the thermograms for various polyamides[44], polyesters[45], and other materials[46].

Polyalkenes. On the assumption that the heat of crystallisation of polyethylene is close to the corresponding value for hydrocarbons with sufficiently high molecular weight, Ke[42] determined the percentage crystallinity of this polymer by finding the ratio of the area of the peak on its thermogram to the peak area for dotriacontane, whose crystallinity was taken as 100%. The degree of crystallinity of polyalkenes was also determined by other workers. Thus Strella[47] describes the thermographic assembly, calculation procedure, and results obtained for crystalline polyethylene and polypropylene. On the basis of the theory that the heat capacities of the amorphous and crystalline sections of the polymer are additive, he used the experimental values of the deviations on the differential curve to calculate the degree of crystallinity for any temperature within the fusion range.

Wunderlich and Kashdan[49] studied specimens of polyethylene crystallised from the melt and isolated in the form of single crystals from solution. The degrees of crystallinity were compared by measuring the areas and heights of the thermographic peaks. In both instances good agreement with dilatometric data was obtained.

The slight lack of rigour in thermochemical calculations from the magnitude of the thermal effect of fusion is due to the fact that the conditions of the process are not isothermal. Chiu[50] described an assembly containing a heating block with two divisions. In the first of these the specimen is heated in the usual way until the required temperature is reached, after which it is immediately transferred to the second, constant-temperature division of the block, and the isothermal crystallisation curve is recorded.

The problems of the thermographic calorimetry of polymers have been examined by a number of authors[51,52]. The thermographic method has been used to study the kinetics of crystallisation of polypropylene[53] and to determine the temperature dependence[54] of the heat capacity of this polymer§. The crystallisation of polyethylene after partial fusion has been studied[55] and problems associated with the influence of the thermal history on the crystallisation of polyethylene have been investigated[56]. Similar problems have also been examined by a number of other workers[14,29,32,52,53,55]. Some thermodynamic aspects of the crystallisation of polyethylene and its copolymers have also been examined[57].

Baltenas and Igonin[58] found that for polyethylene specimens with different degrees of ordering the application of an external pressure of up to 3000 atm leads to an increase in the fusion range and to an increase in the temperature of the endothermic peak by 65–70 deg. This result shows the importance of the study of polymers under pressure; this aspect of thermographic studies has hardly been touched.

A number of factors influencing the shapes and dimensions of the elements of the fusion thermograms for polymers were studied by Ke[59]; he distinguishes factors which are determined by the characteristic features of the preparation of the specimens (the thermal history) and factors which are related to the characteristic features of the experimental procedure (size of specimen, rate of heating, method of introducing the thermocouples, etc.). Similar studies were made for synthetic fibres by Schwenker and Zuccarello[60]. As pointed out by Ke, the shape of the fusion peak gives information on the size distribution of the crystallites. The thermograms which he gives for random ethylene–propylene copolymers reflect the decrease in the percentage crystallinity and the decrease in melting point produced by introducing propylene units into the chain. The author explains this in terms of the effect of lateral methyl groups. In analogous situations, ethyl groups are even more effective. A similar phenomenon is also observed for copolymers of poly(ethylene terephthalate) and isophthalic acid; increase in the concentration of the latter in the copolymer to 40 mole % leads to complete suppression of crystallisation[45].

The thermograms for different crystallising polymers are in general of the same type. Thus the regular features noted for polyalkenes also characterise the thermograms for other classes of polymer.

Polyamides, polyethers, and polyesters. Inoue[61] studied the crystallisation and fusion of various polyamides, poly(oxymethylene), etc., in addition to polyethylene and polypropylene. A detailed study was made of Nylon-6; experiments were carried out to find how the crystallisation is influenced by the temperature of the melt, which determines the number of crystalline nuclei remaining (Fig. 7*a*). For Nylon-6 with high molecular weight and for poly(oxymethylene), two exothermic peaks are observed, attributable to the break in the rate of crystallisation with change in temperature. When a seed crystal is introduced, the crystallisation is complete at the temperature of the first peak (Fig. 7*b*). DTA data were used to estimate the heats of fusion and crystallisation of various specimens and to calculate their crystallinities.

§ The influence of nuclei on the crystallisation of polypropylene was recently studied by Beck and Ledbetter.[48]

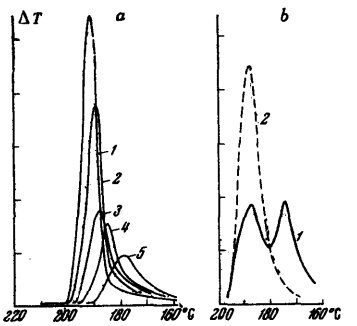


Fig. 7. Dependence of the crystallisation of Nylon-6 on:
a) the initial temperature of the melt: 1) 235°; 2) 245°; 3) 260°; 4) 290°; 5) 320°;
b) the presence (2) or absence (1) of nuclei-forming species.[61]

Gudim[62] used the thermographic method to study physical transformations in caprolactam and polyamide prepared by polymerisation in a vacuum, in an atmosphere of nitrogen, and in air, and also subjected to γ-radiation. The crystallisation and fusion of poly(ethylene terephthalate) were also studied[63]. Differential thermal analysis was used to study the properties of poly-β-propiolactone, prepared by polymerisation in the solid state[64].

The application of the method to organoelemental polymers has also been described[65].

Elastomers. Studies have been made of various forms of natural and synthetic elastomers (natural rubber, gutta-percha, and balata, and various grades of synthetic rubber), in which the fusion of the crystalline phase of the polymers and the conversion of the material from the vitreous state into the highly-elastic state were observed[66,67]. The influence of the rate of heating and the temperature of crystallisation on the melting point of rubber has also been noted[66]. The fusion ranges of the α and β forms of gutta-percha and the influence of the temperature of the melt on their ratio in the polymer were also studied.

Thermographic studies of natural rubber[69], gutta-percha[70], and synthetic chloroprene[71] and divinyl (SKD)[72] rubbers have been made by the authors of the present review. The vitrification, crystallisation, and subsequent fusion of rubbers which had been converted into amorphous forms have been studied, and the optimal crystallisation ranges have been determined. The areas of the peaks on the thermograms have been used to study the kinetics of the crystallisation of natural rubber and the way in which it is influenced by breakdown (milling)[73].

The thermograms of natural rubber show separate fusion peaks for crystallites formed at low temperatures (optimal crystallisation at -25°) and at room temperatures[69]. It has been established that the "high-temperature" crystallites act as nuclei for the low-temperature crystallisation; when the high-temperature crystallites are absent almost no exothermic effect is observed in the region of -25°.

For gutta-percha, cooling curves have been recorded in addition to heating curves. When melts obtained from the α or β forms of gutta-percha are cooled at medium rates, in every instance only the β form crystallises. When

the gutta-percha specimen is annealed at a temperature below the melting point of the β form, only the crystallites of this modification accumulate, whereas when the specimen is kept at a temperature slightly above the melting point of the latter, it is possible to obtain a material which exists almost entirely in the α modification[70].

Two specimens of highly regular divinyl rubber, containing 90% and 81% of the 1,4-*cis*-form, gave thermograms similar to those illustrated in Fig. 2 [72]. The extremely narrow crystallisation range of the first specimen results from the high degree of ordering and uniformity of the crystallites formed.

Recrystallisation processes are readily revealed on thermograms at rates of heating comparable with the rates of these processes. By annealing individual specimens of Nairit [neoprene type (Ed. of Translation)] at various temperatures, it has been possible to observe the increase in the degree of perfection of the crystalline phase and to obtain crystallites in a state close to the equilibrium state[71].

3. Thermographic Manifestation of Polymorphism in Polymers

Some crystallising polymers exist in various crystallographic modifications; we have already mentioned the α and β modifications of gutta-percha. When specimens which have been converted into the amorphous form are heated from low temperatures, the "low-temperature" less perfect form usually crystallises. Subsequently, when these crystals begin to melt, crystallisation of the second "high-temperature" form from the melt may be observed. In clearly defined instances the thermograms show a sharp exothermic effect which as it were separates the two peaks characteristic respectively of the fusion of each crystalline phase (curve *1* in Fig. 8). In less clearly defined instances the exothermic peak may not be so sharp, but the thermograms still show two minima or a "shoulder" on one side of the endothermic peak (curve *2* in Fig. 8). Finally, if the time required for the interconversion of the forms is very much greater than the time taken to pass through the corresponding temperature range in the thermographic experiment, the process is not observed at all on the thermograms. This is the reason for the fact that in the experiments referred to above the conversion of β-gutta-percha into the α form was not observed, whereas at extremely low rates of heating, which are very rarely used in thermographic studies, the thermograms reveal both forms[66,67]. The manifestation of polymorphism on the thermograms of *trans*-polybutadiene was observed by Dannis[68].

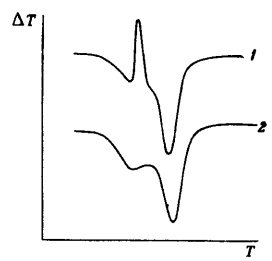


Fig. 8. Characteristic thermograms for polymers exhibiting polymorphism (see text for explanation).

Considerable attention has been paid to the study of the polymorphic transformations in polybut-1-ene, which exists in three modifications: their interconversions have been studied in detail[74]. The metastable tetragonal modification (form II) crystallises from the melt. Form III crystallises from solution. On its thermogram, the endothermic effect of fusion at 94° is converted into a sharp exothermic peak, which corresponds to the transformation of form III into form II. The second endothermic effect at 110° corresponds to the fusion of form II. Annealing of the specimen at appropriate temperatures increases slightly the melting point of each modification[75].

At room temperature, polybut-1-ene is gradually converted from form II into form I [76]; the rate of the conversion of form II into form I is much greater for specimens in the form of films than that for cast specimens[77]. The influence of traces of catalyst (ash) on the rate of the conversion of form II into form I was also studied. This conversion is irreversible[78]. The direct formation of form I during polymerisation has been described[79].

There is lack of agreement as to whether the transformation takes place with the formation of an intermediate melt or by a crystal–crystal scheme.

The phenomenon of polymorphism has been studied by the thermographic method for other series in addition to polyalkenes and dienes. Polyesters formed by adipic acid and *p*-phenylenebisethylene glycol, and also block-polyurethanes based on these materials[80], showed the existence of two polymorphic modifications, described as the α and β forms by analogy with gutta-percha. The heating curve for a polyester specimen which had been converted into the amorphous form and quenched revealed crystallisation of the β form at +12°. It begins to melt at 101–102°, but the exothermic crystallisation of the α form begins at 111°. This is followed by fusion of this form at 152°. The α form is obtained when a melt of the polyester is cooled slowly or when a specimen is subjected to constant-temperature treatment at 120–140°. The corresponding polyurethane which has been converted into the amorphous form crystallises in the β form at a slightly higher temperature and with a smaller thermal effect. The formation of the α form from this melt takes place less intensively, as indicated by the small exothermic crystallisation peak. The results obtained agree with data obtained by X-ray diffraction and infrared spectroscopy.

Of the other polymers, mention may be made of poly(tetrafluoroethylene), on whose thermograms Ke[46] observed two endothermic peaks at 20° and 29°, due to phase transformations in the polymer. The same result was obtained by Slonimskii and Ershova[81].

The thermographic method apparently detects not only the transformation of crystalline phases, but also some transformations in the vitreous state. Thus for polystyrene small thermal effects were observed at about 50°, attributed to hindering of the twisting vibrations of the phenyl groups[82].

4. Structural Transformations in Polymeric Systems

Berg[1], recommending thermography as a method for the phase characterisation of mixtures, points out that it is based on the fact that the temperatures of most phase transformations (and some reactions) are independent of the quantity and quality of the components in the mechanical

mixture. In solutions and alloys, however, the temperatures of phase transformations depend on composition, and thermographic study makes it possible to reveal this dependence. This is also true of polymeric systems, but there are additional considerations, related to the specific features of these materials. The phase analysis of polymeric systems in many instances gives quite definite results. The successful analysis of a mixture of seven polymers has been reported[83].

A random copolymer is a completely homogeneous system, which behaves like a homopolymer, with a characteristic set of properties; it is characterised by a definite vitrification temperature. For crystallising polymers, a decrease in crystallinity is observed on formation of copolymers, due to the non-regularity of the chain. This was examined above for the example of polyethylene containing propylene units. At a certain concentration of co-monomer, crystallisation may be suppressed completely, as mentioned above in connection with studies of polyesters[45]. It has been shown by DTA that polyethylene loses its ability to crystallise at a concentration of any of the co-monomers studied (methyl acrylate, methyl methacrylate, and vinyl acetate) of ~5.5 mole %[84].

Block and graft copolymers exhibit characteristic features which differ from those of random copolymers. In many respects they are similar to physical mixtures of polymers, for which the regular features of the thermograms are determined, as for any two-component or multicomponent systems, by the phase equilibria: the presence and nature of ranges of separation into layers and crystallisation.

Systems formed by a polymer with a substance of low molecular weight. When a polymer and an inert filler are completely incompatible, the effects which they produce on the thermograms are completely independent and differ from those of the individual components only in their intensity. When the components are completely soluble (compatible) in the melt, crystallisation may lead to the formation of mixtures of the eutectic type, or solid solutions, and this, in accordance with the general principles of physicochemical analysis, determines the dependence of the melting points on composition.

Polymers which exhibit a limited compatibility with a substance of low molecular weight occupy an intermediate position. For crystalline polymers in these systems, the endothermic fusion peak is displaced usually towards lower temperatures. If the substance of low molecular weight is also crystalline, the thermogram also shows its characteristic fusion peak. This is illustrated in a paper by Ke[85]. The thermogram for a system in which the component with low molecular weight does not crystallise is shown in Fig. 9, and the thermogram for a system in which both components crystallise is shown in Fig. 10.

Polymer–polymer systems are characterised by thermograms which are determined in general by the same regular features. In the examination of mixtures of polymers, which may be obtained from compatible melts, solutions in a common solvent, or by milling, the question of the physical compatibility of the components of the mixture is of the greatest importance. This problem reduces to the determination of whether the system consists of one or several phases. In the first case the thermograms show one vitrification range and one range of crystallisation or fusion, whereas in the second (in principle at least)

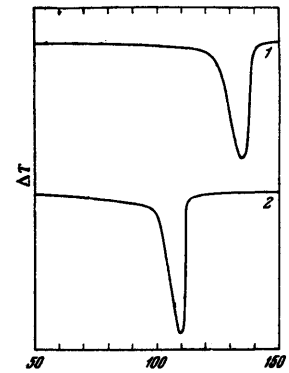


Fig. 9. Fusion of high-density polyethylene: 1) in pure form; 2) containing α-chloronaphthalene.[85]

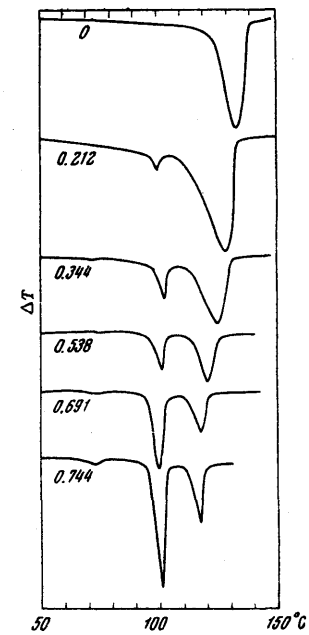


Fig. 10. Influence of phenanthrene on the fusion of high-density polyethylene. The figures next to the curves give the mole fractions of phenanthrene.[85]

the thermograms show several of these elements. Thermography thus provides a method for studying the compatibility of polymers. A study of this type was carried out by Mikhailov and coworkers[86] for the polyethylene–polypropylene system. The authors regarded the formation of two minima on the fusion curve as a criterion of incompatibility. Without objecting in principle to the conclusions reached here, we would point out that the formation of two minima is also observed for homopolymers, for which we cannot speak of compatibility. Thus the presence of several effects is a necessary but not a sufficient sign of non-homogeneity in a system.

Thermograms for the crystallisation of mixtures of the above system were given by Inoue[87]. A noteworthy feature is that the crystallisation of polyethylene and polypropylene takes place in the same temperature range. It

is natural that mixtures of these polymers should show a single crystallisation peak. Nevertheless, these polymers melt at different temperatures, and their non-homogeneous mixtures give separate fusion peaks on the thermograms [86,88].

In other examples the components of the mixtures may have identical melting points, and this feature must always be taken into account in the thermographic analysis of complex mixtures.

Mixtures of high- and low-density polyethylene give a homogeneous melt, but after the latter has solidified, the components melt separately, forming two peaks on the thermograms. An intermediate peak has also been observed [89], and on this basis an equilibrium diagram was constructed for the system, with an extended range of "mixed crystals" [90]. As shown above, however, not every thermal peak need be associated with a separate phase; it may be due to recrystallisation phenomena. A similar view is held by Gray and Casey [29], who consider that the intermediate peak results from annealing. Stafford [83] also studied mixtures of polyethylene with different densities by recording cooling (crystallisation) and heating (fusion) curves. He showed that the DTA method can be used for the quantitative analysis of mixtures.

Inoue [87] studied the crystallisation and fusion of mixtures of polyamides. The degree of crystallinity was determined from the peak areas, and it was concluded that a high degree of crystallinity is attained for the component present in excess. The decrease in the melting point (the peak value) observed for the high-melting component (Nylon-6) was almost imperceptible for the relatively low-melting component (Nylon-11). It should be noted that this last conclusion is not general, since changes in melting points are determined by the relationships between the components, responsible for the form of the fusion diagram of the specific systems.

Block copolymers. The thermograms of block copolymers show features characteristic of each of the polymers forming the blocks. If both are capable of crystallising, and the melting points are different, the thermograms show two separate fusion peaks, as for mechanical mixtures. For the ethylene–propylene block copolymer, Ke [42] showed the dependence of the magnitude of the peaks on the duration of annealing, and from the peak areas he estimated the proportion of each block in the total crystallinity. The same author observed a double exothermic crystallisation peak on the cooling curves, whereas a molten mixture of the corresponding homopolymers, in agreement with Inoue's data [87], gave only one unresolved peak.

Block and stereo-block copolymers with different compositions, obtained from the same components, have been studied [91]. It was found possible to determine the composition of the copolymers from the ratio of the areas of the fusion peaks on the thermograms (Fig. 11). Analogous studies were made by Porter and coworkers [92]. The quantity of crystallites corresponding to each block was found from the heights of the peaks on the thermogram. In spite of the arbitrary nature of this approach, it was found that the ratio of the height of the polyethylene peak to the sum of the heights of both peaks is an almost linear function of the weight fraction for mixtures and copolymers with different compositions. Over a considerable range of change in block ratios, the crystallinity of the copolymer is usually determined by the block present in excess. It is only in the range of comparable ratios that two systems of crystallites are observed simultaneously. This can be illustrated

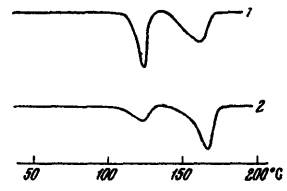


Fig. 11. Fusion of ethylene–propylene block copolymers:
1) 44 mole % ethylene; 2) 13 mole % ethylene. [91]

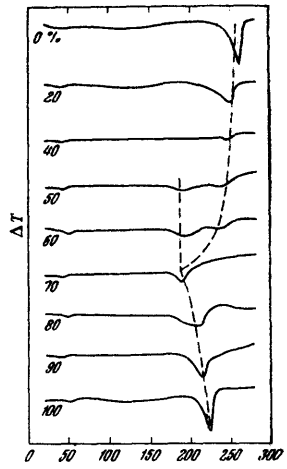


Fig. 12. Fusion of hexamethyleneadipamide–sebacamide copolymers for which a block structure was proposed. The figures next to the curves give the mole percentages of hexamethylenesebacamide. [44]

by an example [44] in which a study was made of poly(hexamethyleneadipamide–sebacamide) copolymers obtained by polycondensation at the phase interface (Fig. 12). The comparatively small displacement of the temperature peaks, shown by the broken line in Fig. 12, indicates, in the opinion of the authors, that the copolymers formed under the reaction conditions are block copolymers (random copolymers, in accordance with Flory's theory, give a much sharper decrease in temperature). The data given in Fig. 12 were used to construct a diagram resembling the eutectic fusion diagrams of binary systems. The "eutectic" composition corresponds to the copolymer containing 70% sebacamide. Block copolymers of the same adipamide with terephthalamide gave a diagram of the non-eutectic type, and this was attributed to the possibility of mixed-crystal formation.

Thermographic studies have been made [93,94] of model block polyesterurethanes, in which one block consisted of an aliphatic polyester and the other consisted of an arylene-containing polyester. The thermogram for a polymer consisting entirely of non-crystallising blocks showed only a jump at the vitrification temperature, after which the differential curve rose very slowly. As the percentage of crystallising blocks was increased, the effect of fusion was

revealed with increasing clarity (the effect is complex due to recrystallisation). In a series of copolymers for which both blocks are capable of crystallising, the regular features observed are similar to those described above for polyamides. In some instances the thermograms were complicated by the phenomenon of dimorphism, characteristic of the polyesters[80].

III. STUDY OF CHEMICAL REACTIONS

1. Thermal Reactions of Polymers

Vulcanisation, isomerisation, and thermal oxidation and degradation are all reactions which can be revealed by thermograms. All these processes are exothermic, except the last: degradation is usually accompanied by absorption of heat. Frequently, it follows one of the other processes (most frequently thermal oxidation) and the exothermic effect is converted into the endothermic effect, just as was observed in the range of crystallisation and fusion of crystals. These effects are observed at much higher temperatures, however, and there is usually no difficulty in distinguishing them. The extent of the exothermic range and the sharpness of the transition from oxidation (or other exothermic process) to degradation is determined by the nature of the polymer, the presence of stabilisers, and the nature of the surrounding atmosphere.

The transformations of phenol–formaldehyde resins were observed by Ravich and coworkers[13]. The exothermic effect at 165° for Resol corresponds to its conversion into Resite, whose thermogram does not show this effect. DTA was used to study[95,96] the vulcanisation of Vibrin-135 — a mixture of poly(glycol maleate) and triallyl cyanurate polymer. The exothermic peak in the range 150–180° corresponds to polymerisation at the double bonds of the polyester and the second allyl group of triallyl cyanurate. The exothermic effect at 300–320° is due to the polymerisation of the third allyl group.

The curing of a large number of commercial products — unsaturated ester resins and epoxide resins — has been studied[97], but the results given are not sufficiently definite. When epoxide compounds react with anhydrides and diamines, an exothermic peak is observed in the range 100–150° (at lower temperatures for the former than for the latter, due to the greater reactivity)[98]. The exothermic peak at 300–400° is considered to be due to the isomeric conversion of the epoxy-groups into carbonyl groups and the start of decomposition.

Unsaturated polyester–styrene copolymers have been studied[99]. The ratio of the exothermic peak areas for specimens cured at room temperature for different periods of time to the peak areas for a specimen studied immediately after preparation provided a measure of the degree of curing (Fig. 13). A similar method was used to study the cure rate of phenol–formaldehyde resins[100]. The rate of vulcanisation of rubber by sulphur has been studied[101] by recording the thermograms for specimens subjected to preliminary partial vulcanisation in a press for different periods of time at 153°. The influence of metal oxides on the vulcanisation of ebonite was also studied[102]. A modification of the thermographic method, which makes it possible to determine the heats of vulcanisation of rubbers, has been proposed[103]. The vulcanisation (under the influence of diamine, benzyl peroxide, or magnesium oxide) of the copolymer of vinylidene fluoride with perfluoroprene

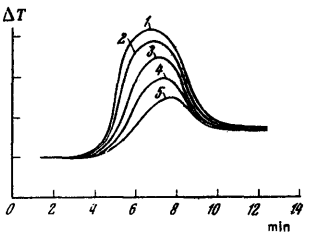


Fig. 13. Polymerisation during the heating of unsaturated polyester–styrene copolymers after hardening for:
1) 2; 2) 3; 3) 4; 4) 5; 5) 6 h.[99]

has been studied, but the thermograms obtained do not appear sufficiently significant[104].

In principle, the thermographic method can also be used to study various polymer-analogue transformations and other reactions taking place with the participation of macromolecular compounds. The thermal effects in the reaction mixtures are studied. Mention may be made of a unique application of the method to study the processes taking place in the water–heat treatment of starch[105,106].

2. Thermal Degradation

Thermographic methods are often used to estimate the thermal stability of polymers. The results of a thermographic experiment differ considerably from the data obtained by prolonged treatment of a polymer at elevated temperatures. This is due to the fact that the thermographic experiment, with its characteristic dynamic temperature conditions, lasts for only a short period and a measurable degree of degradation may be reached at higher temperatures than under the conditions of static tests. Moreover, the shape of the thermogram often depends on the dimensions and shape of the specimen and its degree of dispersion (block or powder), and also on the nature of the surrounding atmosphere. For comparative purposes, however, for example the comparison of a series of specimens, or the study of the influence of stabilisers or other ingredients, the thermographic method can prove extremely useful.

The thermographic method may give information on the mechanism of degradation of polymers. Thus the method has been used to study the degradation of polyethylene (high- and low-density) and polypropylene; it was found that degradation is preceded by oxidation with the formation of hydroperoxides[107]. The thermal behaviour of isotactic polypropylene has also been studied[108]. DTA has been used to investigate the influence of antioxidants on the thermal stability of polyethylene[109].

The thermal transformations of poly(methyl methacrylate), polystyrene, and phenol-formaldehyde resins have been studied[110]; effects associated with degradation of the polymers and secondary decomposition of the breakdown products were observed.

Lee[111] used a variety of methods to study the thermal stability of polycarbonates, and gave the characteristic thermogram for lexan. He considers that the exothermic peak at 300–320° corresponds to oxidation (it almost disappears in an atmosphere of nitrogen), and that the endothermic peak at 340–380° is due to depolymerisation

resulting from reactions such as the separation of hydroperoxides, hydrolysis, the separation of bisphenol, and alcoholysis. The processes of thermal degradation begin at higher temperatures: decarboxylation, dehydration, hydrolysis, dehydrogenation, chain rupture, and the separation of ester (together with possible formation of cross-linkages). With heating in air, these processes correspond to the endothermic peaks at 450–600°. Lee points out that since the initial step in the degradation is oxidation, this process should be inhibited to increase the stability of the polymer, but "pure" degradation may be observed independently of oxidation at higher temperatures. The degradation of block copolymers based on polycarbonate has been studied[112].

Korshak and coworkers studied polybenzimidazoles[113,114] and a number of polyarylates[115], which were shown by thermographic analysis to have a high thermal stability. The temperatures of the start of decomposition of the polyarylates lie in the range 375–465°, and those of the polybenzimidazoles lie in the range 460–520°. Mixed polybenzimidazoles (the diphenyl esters of a mixture of sebacic or terephthalic and isophthalic acids) show a slightly lower thermal stability than the homopolymers. Heat-resistant triazole polymers[116], hexa-allylmelamine polymers, and certain related compounds[117] have been studied.

Studies have been made of the thermal stability, characterised by the temperature where oxidative processes start, for some silicone polymers[118]. Pashchenko[119] has studied organosilicon compounds used as lacquers.

In a study of polymers with inorganic main chains, Andrianov[120] concluded, on the basis of DTA data, that cyclic compounds containing Si, Al, Ti, and Co atoms joined through oxygen have a high stability to elevated temperatures. Opening of the rings takes place above the temperature corresponding to the stability of the organic groups framing the inorganic part of the molecules.

Thermographic methods have been used[121] to study the compatibility of polymethyl methacrylate and octadecylammonium bentonite filler. The latter shows an exothermic effect on the thermogram at 285°, corresponding to the combustion of its organic fraction. This peak is completely suppressed in the presence of 10% poly(methyl methacrylate); the authors regard this as evidence for the compatibility of the polymer and filler.

Studies have been made of the processes taking place when SKN-40 nitrile rubber and phenol–rubber compositions based on it are heated[122]. For SKN-40, an exothermic effect begins at 250°, attributed to rearrangement of the internal structure and the formation of bridges between the molecules. Weight losses are observed above 360° due to oxidative thermal degradation.

The thermal analysis of some polyurethane elastomers[123] and polyester resins[15,124] has been carried out. The stability of a number of fibre-forming polymers has been studied[60] and it has been established that Nylon-6 and polypropylene give only endothermic peaks, indicating depolymerisation, whereas polycarbonate (lexan) and Teflon show both exothermic and endothermic peaks on the thermograms in the degradation range. The thermographic method has been used to study the pyrolysis of wood and its components[125]. DTA has been used to study the influence of inhibitors on the pyrolysis and combustion of α-cellulose[126]. Wood gives an interesting thermogram, which appears as the superposition of the thermograms of its main components — cellulose and lignin. A considerable number of thermograms of natural substances (celluloses, starches, and related compounds) have been published[127]. Studies have been made of the thermal stability and flammability of phenol and epoxide resins used as fillers for paper[128].

It is clear from a large amount of experimental material that the final stage in the recording of the thermograms may be the complete volatilisation of the degradation products (with an endothermic effect), or their combustion (with a sharp exothermic effect), or finally carbon formation, depending on the nature of the polymer and the conditions of the experiment. For an intensive study of the mechanism of degradation it is desirable to combine thermographic methods with study of the change in the weight of the specimen (thermogravimetric studies) and analysis of the decomposition products, for example by chromatography, mass-spectrometry, etc.

3. Reactions of Polymer Formation

A unique application of the thermographic method is in the study of the kinetics and mechanism of the reactions of polymer formation, since these processes involve the liberation of heat.

The thermographic method appears to have been first applied to the study of polycondensation by Brasseur and Champetier[129–131]. In the reaction of ethylene glycol, glycerol, and other polyhydroxy-compounds with phthalic anhydride, the endothermic effect due to fusion (dissolution) of the anhydride is followed by an exothermic maximum due to polyesterification; the water produced at this stage reacts with the excess of anhydride to form the acid. It is only at higher temperatures that the esterification of the dihydroxy- or polyhydroxy-compound by the acid produced leads to the liberation of water; the thermogram then becomes irregular due to the formation of bubbles of water vapour at the thermocouple. If acid is taken at the beginning of the reaction, no exothermic peak is observed on the thermogram.

Thermograms obtained in a study of the formation of phenol–formaldehyde resins[132] showed exothermic effects due to condensation of the original reagents (60–110°) and curing of the resulting resins (168–180°). It is of interest to compare the thermograms recorded at different component ratios (Fig. 14). The thermographic method has been used to study the formation of alkylphenolic resins[133].

The thermographic method has also been used to study the mechanism of polymerisation[134] for triallyl cyanurate and triallyl isocyanurate. Triallyl cyanurate gives peaks at 100° and 160–220°. The first was attributed to the reaction of two of the double bonds, and the second to polymerisation at the third double bond with the simultaneous

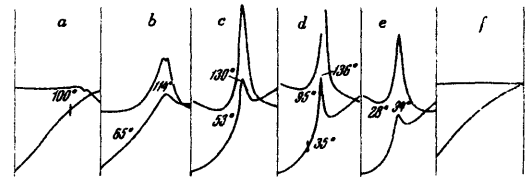


Fig. 14. Action of heat on phenol–formaldehyde mixtures with phenol concentrations (%):
a) 10; *b*) 30; *c*) 58; *d*) 80; *e*) 90.[132]

conversion of cyanurate into isocyanurate. In triallyl isocyanurate all the double bonds are polymerised at the temperature of the first exothermic peak.

The formation of macromolecular compounds by polymerisation under the influence of radiation has been studied. Since the process is exothermic, it has often been studied by measuring the increase in temperature in general [135] and by the thermographic method in particular. In the study of the polymerisation of formaldehyde in the solid state under the influence of γ-rays [136], it was found that at certain temperatures and intensities of irradiation the reaction acquires the character of a thermal explosion. The analogous reaction of acetaldehyde has also been studied [137].

DTA has been used to study the polymerisation, initiated by irradiation, of cetyl methacrylate, *N*-methylsuccinimide, and *N*-vinylcaprolactam in the solid and liquid states [138]. The reaction takes place smoothly or explosively, depending on the conditions. The radiation polymerisation of crystalline trithiane has been studied [139].

Kargin and coworkers [140-142] used the thermographic method to study the polymerisation taking place when certain monomers were heated below their melting points in the presence of magnesium vapour as initiator. They noted that this process takes place at temperatures close to the phase transformations of the monomer and is explosive in character. Thus the thermogram for the acrylonitrile–Mg system shows "spikes" on the differential curve at -165° or -135°. These temperatures correspond to exothermic maxima on the thermogram for pure acrylonitrile.

In the works cited, the thermographic method was used for the direct observation of polymerisation in the solid state, but it has also been used to characterise the polymers obtained [143].

IV. THERMOGRAPHY AND RELATED METHODS OF STUDY

The thermogravimetric method. The method involving the periodic weighing of a specimen kept at a definite temperature is often used to estimate the thermal stability of a polymer and to study the kinetics of its decomposition. The automatic recording of the change in weight in a controlled atmosphere, particularly under vacuum, both under isothermal conditions and with regular increase in temperature, has undoubted advantages [144]. In the latter circumstance the thermal conditions correspond to those used in the thermographic method, so that it is possible to record thermographic and thermogravimetric curves simultaneously; this method is used in the study of minerals [145]. The assembly may also record the linear contraction of the specimens [146] (see also Mashintsev and coworkers [147]). In another successful development [148], the apparatus records not only the simple and differential temperature curves and the weight curve, but also a differential curve characterising the rate of change in weight. This apparatus has been called a derivatograph.

Thermography with recording of the gas liberation. The formation of gas during the thermal degradation and certain other reactions of polymers makes it possible to study these processes from the dynamics of gas liberation. Both manometric [149,150] and volumetric methods can be used. An advantage of the volumetric method over the manometric method is that the pressure is kept constant, so that it does not oppose the reaction. The combination of the thermographic method with automatic recording of the gas liberation was developed for substances with low molecular weights [151], but it can also be applied successfully to polymeric materials. The possibility of carrying out the recording at reduced pressure is extremely valuable [152]. Although this method has not yet been applied to polymers, we would like to point out its promising possibilities. It should be noted that the volumetric and thermogravimetric methods do not always give concordant results. For example, in the degradation of polymers the gases and non-condensing vapours form only one source of the loss in weight; condensing volatile decomposition products do not produce a change in volume.

The combination of thermographic methods with mass-spectrometry is extremely fruitful. Under smooth heating conditions, it is possible to record the thermograms and either to obtain the mass spectrum (with rapid scanning) at various temperatures or to record continuously the ion current — either the total current or the current corresponding to a given ion, for example H_2O^+ (m/e = 18). In one scheme [153] a milligramme specimen is placed in a miniature furnace mounted directly in the ion source of a mass-spectrometer of the time-of-flight type. The decomposition is carried out under the extremely high working vacuum conditions of the instrument (about 10^{-7} mmHg). In another development [154], the gases formed on decomposition pass into the mass-spectrometer along a tube from a removable heating block in which any desired pressure can be maintained. In the latter case, however, retardation of the mass-spectrometric peak relative to the thermographic peak may be observed, the retardation being greater, the higher the pressure and the greater the "dead volume" of the system. This method, which has been tested for substances of low molecular weight, appears quite promising for the study of polymers. The same is true of the combination of thermographic methods with gas chromatography.

Thermography combined with microstructural studies. The thermograms for micro-quantities of a substance can be recorded directly on a microscope slide, heated by a linear programme on a special heated microscope stage [155]. It then becomes possible to make simultaneous observations, to take photographs at intervals, or even to record a cine-film. A correlation is thus established between the structural changes observed in the microscope and the thermal effects on the thermogram. This method, which has been used successfully, in particular, to study the phase structure of triglycerides, also appears promising for the study of polymeric materials. The combination of the widely used microscope observation of structures and their transformations with thermographic characterisation of the polymers appears extremely promising.

Thermographic and thermomechanical methods for studying polymers. Thermomechanical curves [157] are widely used in the study of polymers [158]. The method most similar to the thermographic method is that in which the temperature is altered by a linear programme and the deformation of the polymer takes place under the influence of a continuous load [159]. Automatic recording of the deformation on deformation–time coordinates or, more particularly, deformation–temperature coordinates [160,161] makes it possible to compare the curves obtained with thermograms recorded under the same thermal conditions. An assembly has been described, in which the

specimens used to obtain the thermograms and thermomechanical curves are heated simultaneously in the same block.

The thermomechanical curves for amorphous polymers can be used to determine the temperatures of vitrification and flow. The thermograms give the vitrification point but do not reveal the point corresponding to conversion into the fluid state. The thermomechanical curve records any change in the state of the polymer, if this change is associated with a change in its deformability (under a varying load)[162]. The thermographic method records a change in the state of the substance through its thermal properties, and the thermomechanical method records a change in state through the mechanical properties. In specific instances these methods may show different sensitivities to a change in state, so that the two methods supplement one another.

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KINETICS AND MECHANISM OF THE BECKMANN REARRANGEMENT OF ALICYCLIC KETOXIMES UNDER THE CATALYTIC ACTION OF SULPHURIC ACID AND OLEUM

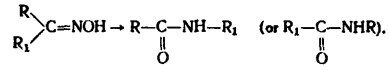
M. I. Vinnik and N. G. Zarakhani

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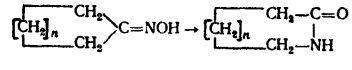
I. INTRODUCTION

In 1886 Beckmann[1] first carried out the conversion of oximes into acid amides. This reaction is called the Beckmann rearrangement. In the rearrangement of the ketoximes *N*-substituted amides of carboxylic acids are formed:



The Beckmann rearrangement was at first used only under laboratory conditions as a convenient and simple preparative method and as a method for establishing the structure of ketones. This reaction made it possible to synthesise a large number of amides, and also various amino-acids, which either were unknown or were obtained by complex processes of poor efficiency.

Recently the Beckmann rearrangement of a series of cyclic aliphatic ketoximes has attained great importance as an industrial method of obtaining lactams:



The rearrangement of cyclohexanone oxime into ϵ-caprolactam is of special importance. The industrial production of the lactam of ϵ-aminocapronic acid is one of the multi-tonnage processes of contemporary chemical industry. Wallach[2] obtained ϵ-caprolactam from cyclohexanone oxime under the catalytic action of sulphuric acid in 1900. ϵ-Caprolactam is the raw material for the production of one of the most important products of contemporary synthetic chemistry — caprolactam polyamide.

Lactams with a greater number of carbon atoms than ϵ-caprolactam also find application in industry, since they have been used as the basis of syntheses of polyamide resins with different physicochemical and mechanical properties.

The Beckmann rearrangement is an acid–base process and proceeds under the catalytic action of a large quantity of the reagents. The catalysts for this reaction are protic and aprotic acids. Concentrated sulphuric acid is usually employed, but phosphoric acid, phosphorus pentachloride, aryl sulphonyl chlorides, aluminium chloride, hydrogen bromide, and hydrogen fluoride are also used as catalysts. "Beckmann mixture" is an active catalyst for the rearrangement; it consists of a saturated solution of hydrogen chloride in glacial acetic acid, to which is then added ~ 20% acetic anhydride. This reagent is used under conditions when the oxime reacting is insoluble in other solvents.

Because of the great theoretical and practical interest of the Beckmann rearrangement, the literature devoted to an explanation of its mechanism is voluminous. There are