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A NEW THERMALLY STABLE COPOLYMER OF FORMALDEHYDE

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Abstract—By polymerizing anhydrous formaldehyde and dimethylketene in the presence of anionic catalysts (e.g. $P(C_6H_5)_3$), it is possible to obtain a copolymer having prevailingly a polyoxymethylenic structure, containing ester units of the type

$$\begin{array}{c} H_3C \quad O \\ | \quad\quad \| \\ -C-C-O-CH_2- \\ | \\ H_3C \end{array}$$
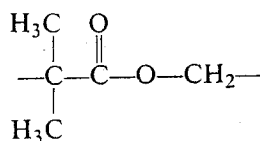
These units have a considerable effect on the thermal stability of the polymer since they hinder the complete unzipping of the polyacetalic chains.

The chemical behaviour and the physical-mechanical properties of a copolymer having a content of 4 per cent by weight of dimethylketene, are compared with those of the acetylated homopolymer and of the trioxane–dioxolane copolymer.

For a few years, research has been directed towards the study of the polymerization of formaldehyde both as momoner and as cyclic trimer, because of the excellent mechanical properties of polymers containing long oxymethylenic sequences. The most important problem to be solved when preparing polyoxymethylenic polymers is to achieve thermal stability, and so to avoid chain degradation and consequent regeneration of the monomer. This problem was practically solved in two ways:
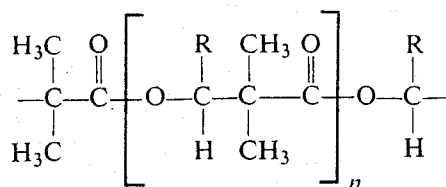
(1) Products obtained by homopolymerizing formaldehyde, either as monomer or as its cyclic trimer, can be stabilized by modifying end-groups of the macromolecules; for example hydroxylic end-groups can be converted to either ester or ether groups.[1]

(2) The degradation started at the chain ends can be stopped by introducing sequences of adjacent carbon atoms in the polyacetalic chain; in fact any C—C bond hinders the β-decomposition that characterizes unzipping.[2]

Obviously in the latter case, various solutions of the problem are possible, but some difficulties must be overcome:

(i) In order to maintain the exceptional mechanical properties of the oxymethylenic polymers, the copolymer structure must be little different from that of the formaldehyde homopolymer.

(ii) In order to obtain a homogeneous polymer, the sequences of adjacent carbon atoms must be well distributed in all macromolecules.

(iii) The high processing temperature of the acetalic resins requires that the monomer units derived from comonomer have high thermal stability.

Copolymers of practical interest have been obtained so far only starting from the cyclic trimer; in particular, commercial production of trioxane–ethylene oxide copolymer has already started.[2] Investigations have been made on the copolymerization of anhydrous formaldehyde with other monomers but, as far as we know, satisfactory results have not been described yet. The reactivity of anhydrous formaldehyde is generally so high, in comparison with that of other monomers, that it is very difficult to obtain a polyacetalic chain of sufficient length, containing a few percent of C—C sequences. The little information existing in patent literature refers to the use of comonomers polymerizable by cationic catalysts,[3] but no information is available on the thermal stability of the copolymers obtained. During our research on the reactivity of carbonyl compounds, we observed that ketoketenes can be easily polymerized in the presence of acid and basic catalysts. In particular the study of the copolymerization of formaldehyde with dimethylketene (DMK) seemed justified.

Under the influence of organometallic compounds (lithium alkyls, zinc alkyls and lithium alcoholates), dimethylketene easily yields alternating copolymers with compounds containing carbonyl groups. Aldehydes[4] ketones[5] and formates[6] polymerize by opening of the C=O bond; for example, in the case of an aldehydic compound R—CHO, crystalline macromolecules are obtained, characterized by the presence of sequences of the type:

$$\underset{H_3C}{\overset{H_3C}{\underset{|}{\overset{|}{C}}}}\overset{O}{\overset{||}{C}}\left[\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{O-C}}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-C}}\overset{O}{\overset{||}{-C}} \right]_n \underset{\underset{H}{|}}{\overset{\overset{R}{|}}{O-C-}}$$

Moreover, the symmetrical structure of the monomeric unit of dimethylketene (1)

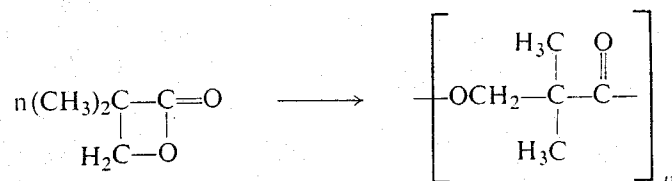$$\underset{H_3C}{\overset{H_3C}{\underset{|}{\overset{|}{-C}}}}\overset{O}{\overset{||}{-C-}}$$

1
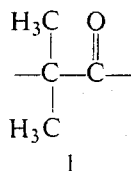
and the thermal stability of some alternating copolymers having a polyester structure,[7] suggested that the thermal stability of a formaldehyde–dimethylketene copolymer might be remarkable.

The experimental results have proved that it is possible to obtain copolymers in which the monomeric units of formaldehyde and of dimethylketene alternate, giving rise to ester groups. By adopting suitable reaction conditions, it is possible to control the growth of the chains so as to favour the formation either of a random or block or alternating copolymer. In the first two cases, it is generally possible to attribute the following structure to the macromolecules obtained:

$$-CH_2O-CH_2O-CH_2O\left[\overset{O}{\overset{||}{C}}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-C}}-CH_2O \right]_n CH_2O-CH_2O-$$
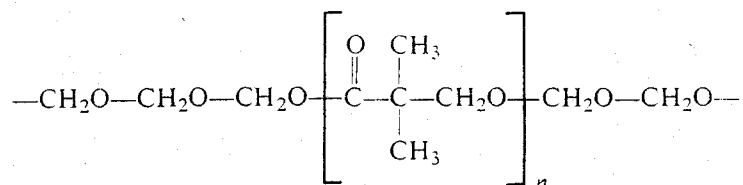
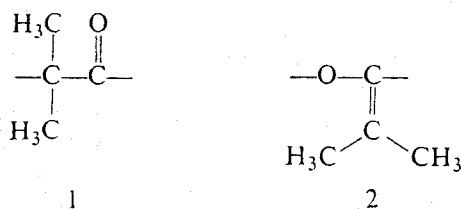where n can be 1 or a higher number.

Obviously, the possibility of modifying the acetalic structure of polyformaldehyde within wide limits may lead to a thermally stable polyoxymethylene having physical and mechanical properties near to those of the formaldehyde homopolymer, or to a linear polyester having the same structure as the polycondensation product of hydroxy pivalic acid[8] or of the pivalolactone polymer:

$$n(CH_3)_2\underset{\underset{\displaystyle O}{|}}{\overset{}{C}}\!\!-\!\!\underset{\underset{\displaystyle O}{|}}{\overset{}{C}}\!\!=\!\!O \longrightarrow \left[\!-OCH_2\!-\!\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H_3C}{|}}{C}}\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\right]_n$$

In this communication we report some results concerning the synthesis and the properties of the copolymer prevailingly polyoxymethylenic in structure.

Copolymerization of anhydrous formaldehyde with dimethylketene

The copolymerization of formaldehyde with dimethylketene is catalysed by basic compounds; the tertiary amines and phosphines which are good catalysts for the homopolymerization of formaldehyde, are particularly active. Also dimethylketene alone reacts, under analogous conditions, forming oily or solid homopolymers;[1] in this case however, the two possible monomeric units 1 and 2

$$\underset{\underset{\displaystyle H_3C}{|}}{\overset{\overset{\displaystyle H_3C}{|}}{-C}}\!-\!\overset{\overset{\displaystyle O}{\|}}{C}- \qquad\qquad -O\!-\!\overset{\overset{\displaystyle C}{\|}}{\underset{\underset{\displaystyle H_3C\quad CH_3}{}}{C}}-$$

1   2

are enchained irregularly, whereas in the polymerization with formaldehyde, dimethyl-ketene is exclusively added by opening of the carbon–carbon double bond. It is interesting to note that the compounds that catalyse the homopolymerization of both monomers (e.g. many metal alkyls) form either thermally unstable copolymers having an irregular structure or mixtures of two homopolymers. The distribution of dimethyl-ketene units in the copolymer in any case depends on the catalyst used; some tertiary phosphines, such as triphenylphosphine, lead to considerable structural regularity. The conversion of formaldehyde is generally very high, while that of dimethylketene varies according to the operating conditions, especially temperature. Even although temperature can vary within very wide limits, the operating temperature should not exceed 20° in order to avoid the partial conversion of dimethylketene into oligomers and the formation of oily copolymers. If the reaction is carried out at 0°, about 80 per cent of the ketene enters into the polyoxymethylenic chains.

In order to secure good reproducibility, well defined operating conditions must be chosen. Satisfactory results have been obtained by feeding continuously both monomers (anhydrous formaldehyde as gaseous form, and dimethylketene in the liquid phase) into the reactor already containing the catalyst solution. The nature of the solvent influences the physical condition of the polymer. In aliphatic solvents (e.g. n-heptane),

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the polyacetalic copolymer is completely insoluble and separates in a powdery form which can be easily filtered and dried. The use of low-boiling solvents (e.g. n-butane) allows an easy thermal control of the reaction, which is highly exothermic. Some results are reported in Table 1.

TABLE 1. COPOLYMERIZATION OF FORMALDEHYDE AND DIMETHYLKETENE IN HYDROCARBON SOLVENTS

	Feeding rate of CH_2O (a) (g/min)	Dimethyl-ketene (b) (ml)	Solvent (ml)	Catalyst (mmoles)	Temp °C	Polymer obtained g	Dimethyl-ketene content in the polymer % (c)
1	2·7	4	butene 500	$(C_4H_9)_3N$ 0·3	− 5	40·5	3·2
2	2·7	4	n-heptane 500	$(C_4H_9)_3N$ 0·3	−10	34	5·3
3	4·2	6	n-heptane 1000	$(C_6H_5)_3P$ 1	−12	58·5	4·6
4	3·9	4	toluene 550	$(C_6H_5)_3P$ 1	0	50	4·9
5	3·9	4	cyclohexane 550	$(C_6H_5)_3P$ 0·1	10	53	4·2
6	1·3	2	n-heptane 550	$(C_6H_5)_3P$ 0·1	− 5	20	4·6
7	2·7	4	n-heptane 550	$(CH_3)_3N$ 0·12	−10	40·5	3·6
8	2·7	20	n-heptane 550	$(C_2H_5)_3N$ 0·12	−10	41·9	16
9	2·9	3	n-heptane 550	$(C_6H_5)_3P$ 0·1	20	29·5	1·6

(a) Reaction time: 15 min.
(b) About ⅓ of the dimethylketene is introduced at the beginning, and ⅔ are fed continuously during the polymerization.
(c) Determined on the polymer after removal of the fraction unstable at 165°.

The problem of the purification of the crude polymers is simplified by the nature of the catalysts: for example it is possible to remove ash by washing with aqueous ammonia solution at 50°.

Structure of the formaldehyde–dimethylketene copolymer

The presence of dimethyl-ketene units in the copolymer having mainly a polyoxy-methylenic structure, has been revealed by the IR spectrum; in addition to the typical absorption bands of the oxymethylenic bonds, other bands, characteristic of the ester groups, are observed at 1738, 1165, 867 and 763 cm^{-1}. On the contrary, the absorption band at 1081 cm^{-1} (attributed to the ketenic units polymerized via the C=O bond[9]), and the band at 1669 cm^{-1}, characteristic of a sequence consisting of several ketenic units polymerized in the C=C bond) are absent (Fig. 1).

The DMK content was determined both by IR analysis on the basis of the absorption band at 1738 cm^{-1} (using as standard the alternating formaldehyde–dimethylketene copolymer (Fig. 2)) and by analysis according to the Romijn method,[10] by measuring the aldehyde formed in the acid hydrolysis of the polymer.

The copolymer with low DMK content is homogeneous in composition. This can be deduced from the following observations:

(1) Only a small fraction (generally below 10–12 per cent) can be removed by treatment with a hot aqueous solution of ammonia. This fraction contains homopolymers of formaldehyde, polyoxymethylenic chains having only one monomer unit derived from dimethylketene, and segments having a polyoxymethylenic
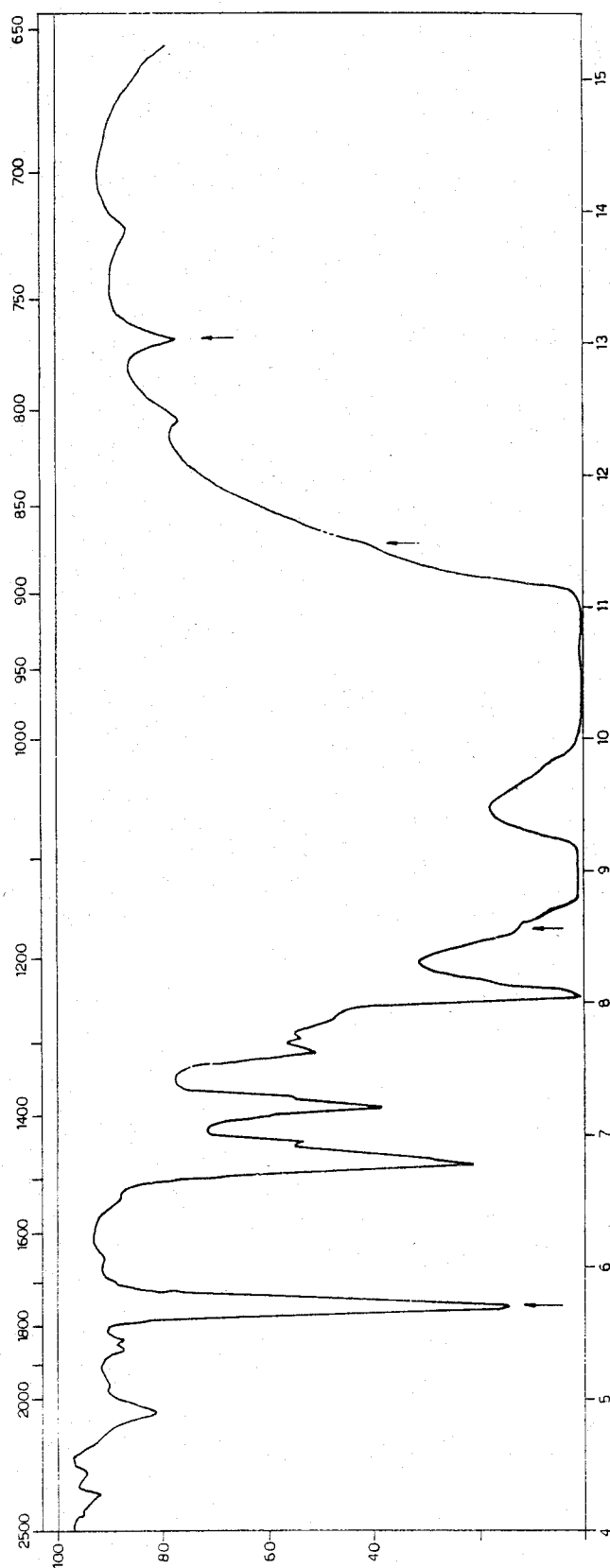
FIG. 1. IR spectrum of a formaldehyde–dimethylketene (DMK 4 per cent) copolymer—film 0·1 mm.
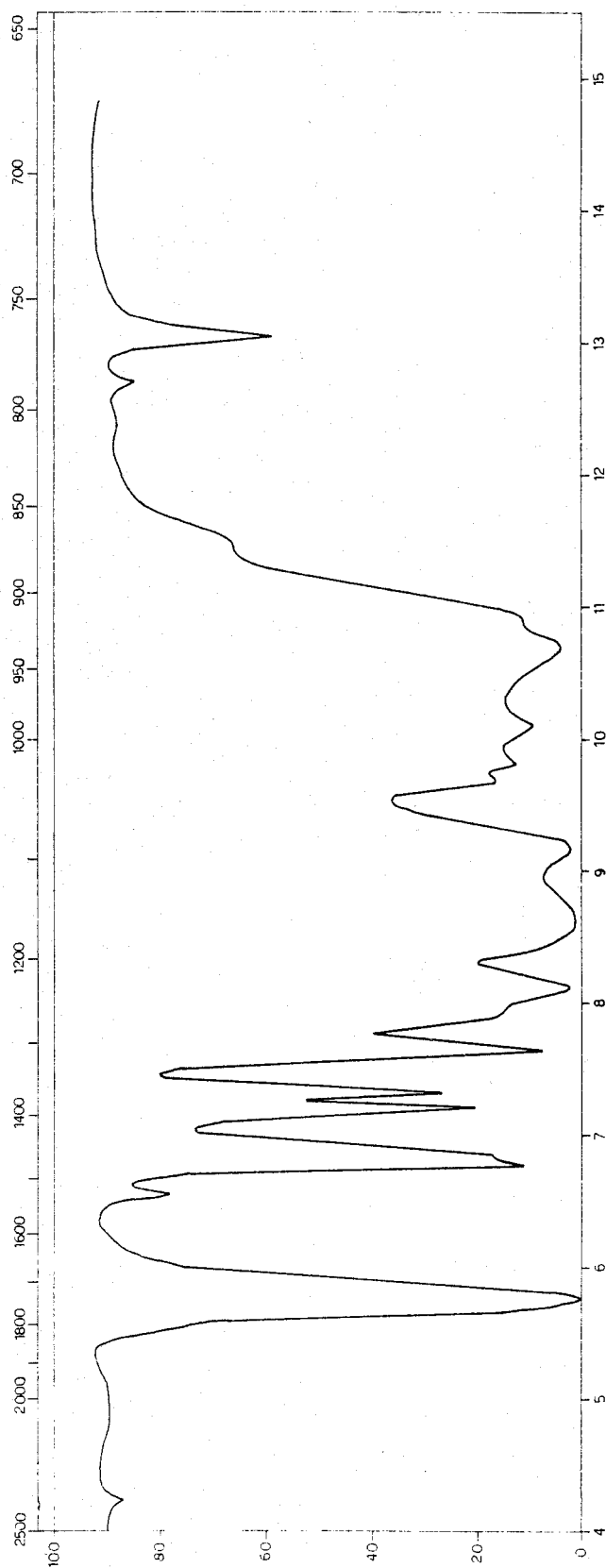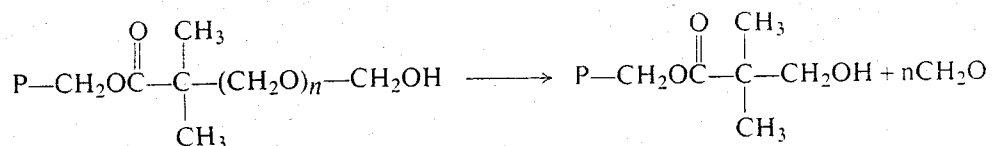
FIG. 2. IR spectrum of a formaldehyde–dimethylketene copolymer mainly having an alternating structure (with about 10 per cent of polyoxymethylenic sequences)—film 0·1 mm.

structure probably constituting the ends of the chains of copolymer molecules containing several DMK units. These segments are degraded according to the reaction:

$$P-CH_2O\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-(CH_2O)_n-CH_2OH \longrightarrow P-CH_2O\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH + nCH_2O$$

(2) Polymer fractions soluble in boiling chloroform are practically absent; therefore molecules completely or mainly consisting of alternate monomer units of the two types are absent.

The residue after treatment with hot aqueous NH_3 contains a low concentration of hydroxylic end groups (determined according to Brown);[11] this concentration (0·03–0·05 mole/kg of polymer) is practically the same for all copolymers having equal viscosity and dimethylketene content. The absence of formaldehyde homopolymers after heating in an alkaline medium is confirmed by the complete stability of the molten product *in vacuo* at 180°; it is known that under these conditions polyoxymethylene hydrates are rapidly degraded.

The regularity of distribution of the monomer units in the low DMK content copolymers (1–5 per cent by weight) can be approximately evaluated by examining the spectrum in the region between 800–1000 cm^{-1}, and more precisely by examination between 900–905 cm^{-1}; in fact a band characteristic of the length of the oxymethylenic sequences falls in this region.[12] For the copolymers examined, the intensity of this band increases regularly with a decrease in the average dimethylketene content; therefore it can be assumed that the average length of the oxymethylenic sequences increases with the same regularity. The uniform distribution of ketenic units in the copolymers with low dimethylketene content is also demonstrated by thermal analysis (Fig. 3). The behaviours during the heating of the homopolymer and of a copolymer with a low DMK content are distinctly different.

In copolymers with a higher DMK content (8–12 per cent by weight), distribution of the ketene in the chains tends to be less regular. After heating the polymer to a high temperature (150° in air) and destroying the acetalic sequences, a waxy residue is obtained; this material consists mainly of chain segments with a polyester structure.

This result is indicated in Fig. 4, which shows, for comparison, the spectrum of oligomers obtained by condensation of hydroxypivalic acid.[13] The average degree of polymerization of the oligomers derived from polyester sequences (evaluated with the Mechrolab 301 osmometer) ranges between 3 and 6.

The melting temperature of the copolymer varies with its composition: it ranges from 168–174° for copolymers containing little DMK to 150–155° for those containing about 10 per cent DMK. Polyester sequences prevail for even higher ketene contents (10–15 per cent) and the product does not show a characteristic melting point.

The analysis of the X-ray spectrum leads to analogous conclusions. The X-ray crystallinity of a copolymer containing few DMK units is only slightly less than that of a formaldehyde homopolymer treated similarly. For dimethylketene contents of 8–10 per cent by weight, the crystallinity is reduced considerably; the characteristic crystallinity of the alternating dimethylketene–formaldehyde copolymer is, however, not evident in these copolymers.
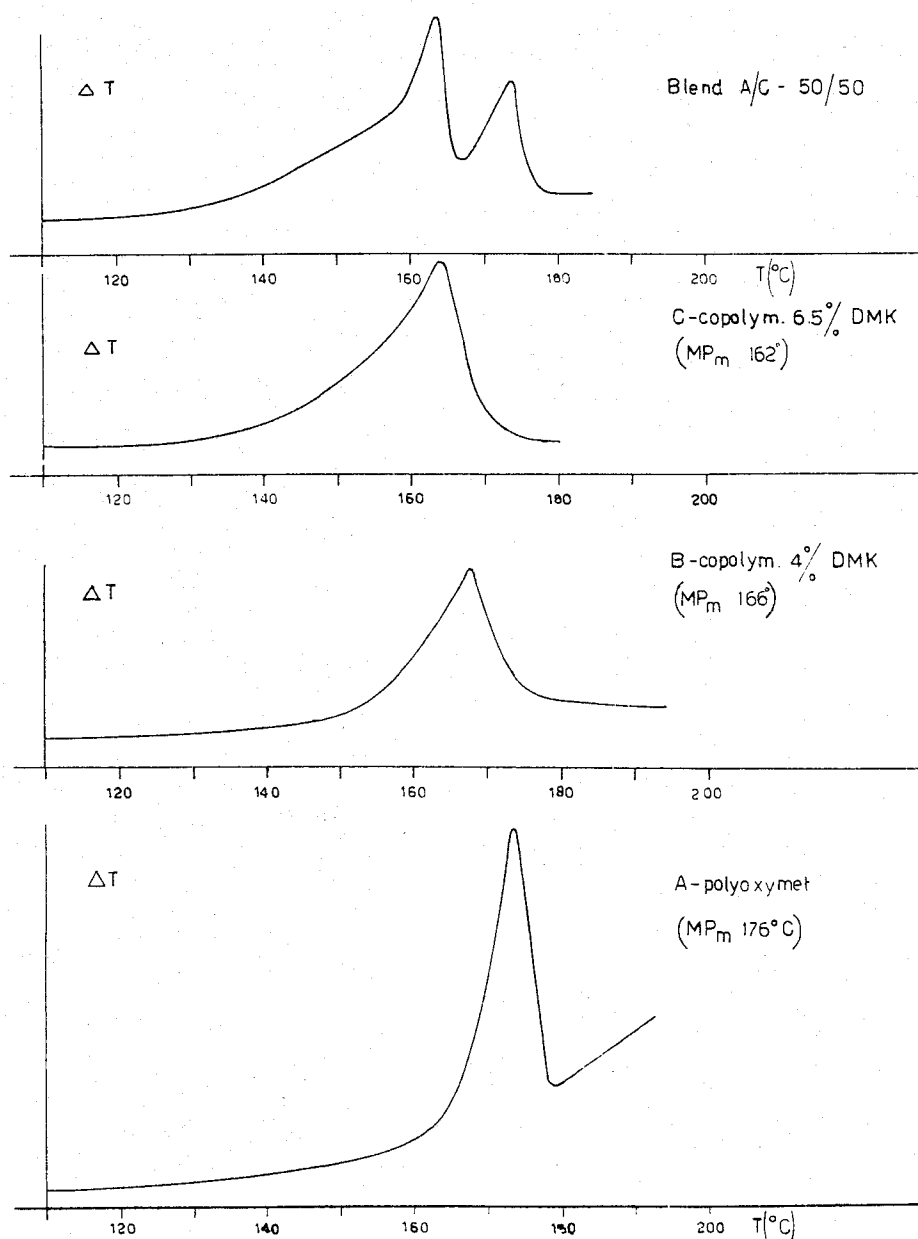
Fig. 3. Differential thermal analyses of polyoxymethylene diacetate (polymer A), of a formaldehyde–dimethylketene copolymer with 4 per cent of DMK (copolymer B), of a co-polymer with 6·5 per cent of DMK (copolymer C) and of a blend (A+C) (MP_m = m.p. at the polarizing microscope).

Thermal stability of the formaldehyde–dimethylketene copolymer

The most important requirement for the technological application of a polymer with polyacetalic structure is high thermal stability. Generally, stability is assessed from weight loss in air at 200° in the presence of antioxidants and of suitable nitrogen containing stabilizers, or from degradation rate in nitrogen at 220° for unstabilized products.[14]

A comparison between the thermal stabilities of the formaldehyde–dimethylketene copolymer and of the main oxymethylenic polymers is reported in Table 2. The degradation rate of the formaldehyde–dimethylketene copolymer, measured in air and nitrogen, is intermediate between those of the trioxane–cyclic ether copolymer
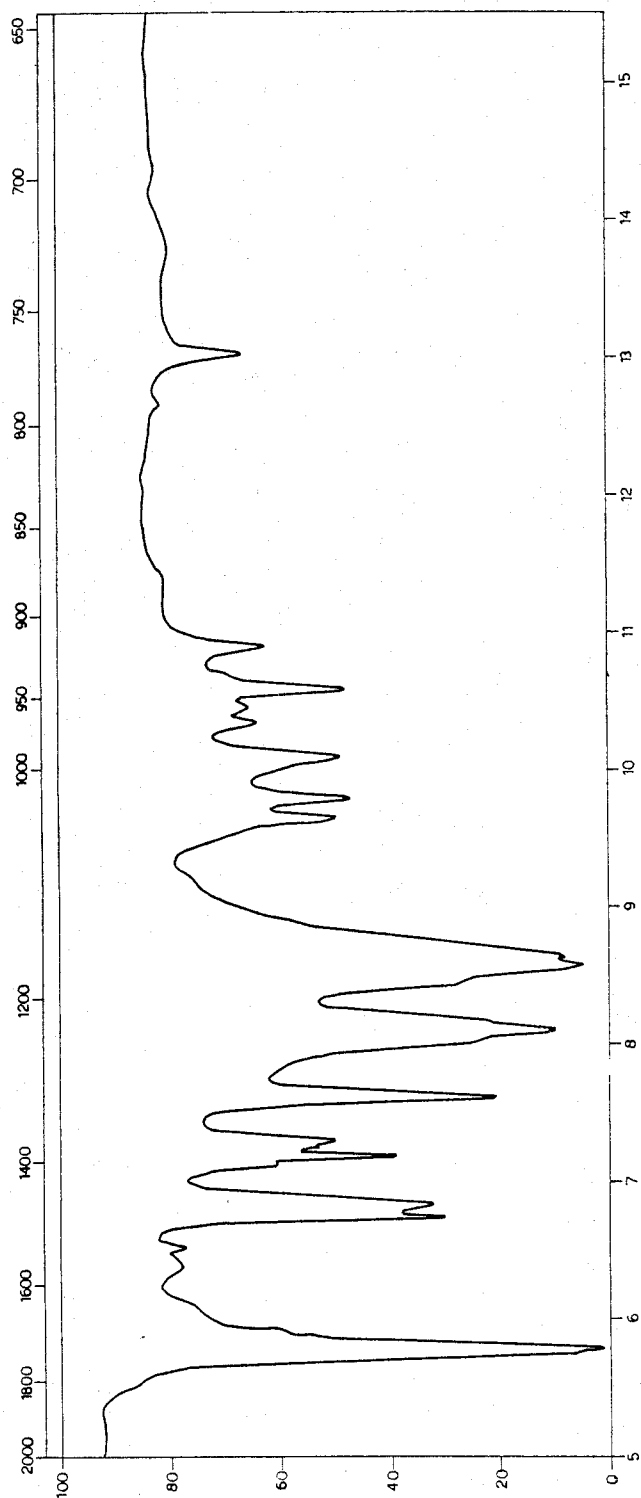
Fig. 4. (a) Ir spectrum of a polymer of β-hydroxypivalic acid having a low degree of polymerization (capillary film).
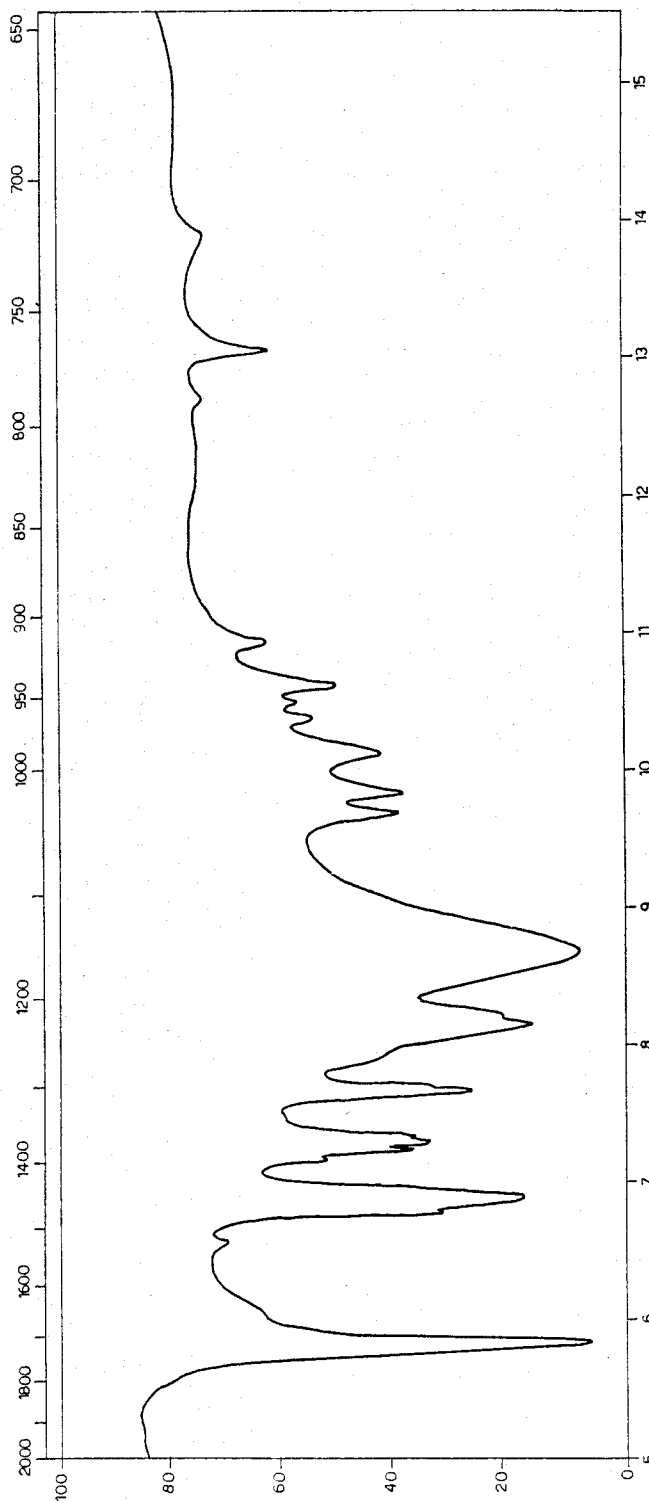
FIG. 4. (b) IR spectrum of the residue from the thermal degradation of a formaldehyde copolymer (about 10 per cent of DMK).

TABLE 2. THERMAL STABILITY OF SOME POLYMERS HAVING POLYOXYMETHYLENIC STRUCTURE

Polymer (a)	% comonomer	M.p. °C	Weight loss in air (% at 200°C in 30')	K^{222} in nitrogen (b) (% per min)
Polyoxymethylenediacetate	—	176	0·8–1·4	0·12–0·15
Trioxane–ethylene oxide copolymer	2·5±1	170	0·2–0·5	0·03–0·05
Formaldehyde–dimethylketene copolymer	4·0±1	167	0·5–1·0	0·08–0·1

(a) All the copolymers examined had an inherent viscosity of 0·6 (determined in dimethylformamide at 150°).

(b) Measured by Eyraud thermogravimetric scale and calculated according to McDonald.[14]

(Celcon-type of American Celanese) and the formaldehyde homopolymer stabilized by acetylation of the end groups (Delrin-type of Dupont).

It is of particular interest to note that, whereas at 220° the differences in stability (measured in nitrogen) of the acetylated homopolymer and of the formaldehyde copolymers are too small to be clearly detectable, the weight loss curves plotted at
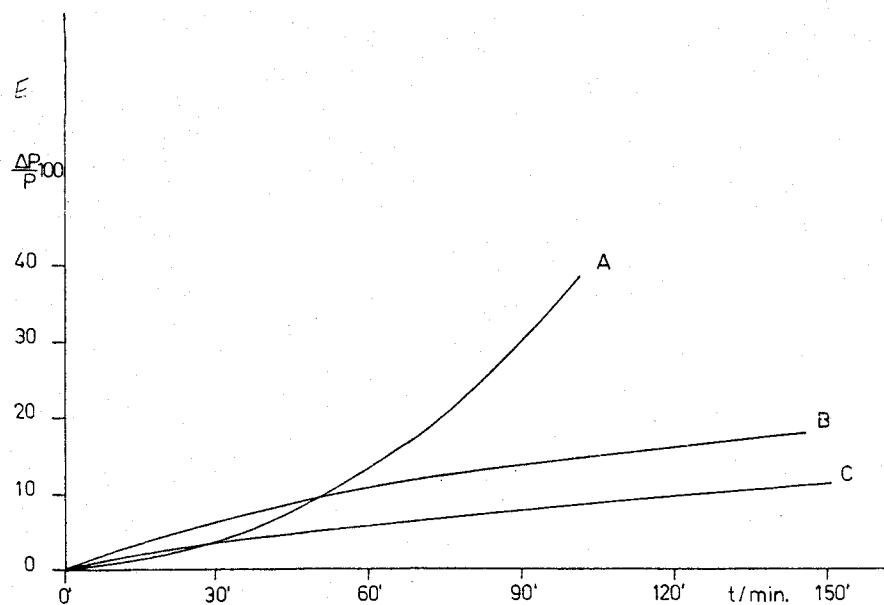

FIG. 5. Comparison of the thermal degradation curves of a formaldehyde–dimethylketene copolymer and of polyoxymethylenediacetate

A   homopolymer (+biuret) at 250° under N_2.
B   copolymer 4 per cent DMK at 250° under N_2.
C   copolymer 4 per cent DMK (+antiox.) at 220° in air.

250° show that the two types of macromolecule behave differently during degradation. Figure 5, in which the stability of polyoxymethylenediacetate is compared with that of a formaldehyde–dimethylketene copolymer (having the same viscosity), shows that autocatalysis during degradation is evident only for the homopolymer.

It must be assumed that acid groups, which can be produced from the ester bond in the depolymerization of the CH_2O–DMK copolymer, are present at a very low concen-

tration: such groups do not exert a profound effect on stability of the chain towards acidolysis. Further evidence for the thermal stability of the ester sequences is given by the complete stability of the formaldehyde–dimethylketene alternating copolymer up to 260°; this is also the limit-temperature for the stability of the C—O bond in the polyoxymethylenic chains.[15]

Analogous conclusions on the thermal stabilities at high temperatures of the formaldehyde homopolymer and copolymer with dimethylketene can be drawn from viscosity and molecular weight data. Samples free from thermal stabilizers were heated for a long time in air at 200° in the presence of antioxidants; the reduction in molecular weight of the copolymer is generally lower than that for the homopolymer.

Chemical stability of the formaldehyde–dimethylketene copolymers

The stability towards oxidation of the formaldehyde–dimethylketene copolymer (without addition of antioxidants) is not substantially different from that of a polyoxymethylenediacetate, having the same degree of crystallinity. Products having a lower degree of crystallinity and characterized by a low melting point, show a lower resistance to oxidation; this can be explained if oxygen can more easily attack the amorphous fraction. For example, a copolymer having a dimethylketene content of about 6 per cent (m.p. 163°) in air at 150° shows an induction period of about 1 hr; yet polyoxymethylenediacetate and a copolymer having a crystallinity of 75–80 per cent, show an induction period of 3–4 hr.

In its resistance to hydrolysis and to acidolysis, the formaldehyde–dimethylketene copolymer can be compared with the formaldehyde homopolymer or its copolymers with cyclic ethers; thus appreciable degradation is not observed while boiling an aqueous acid suspension (pH $\geqslant$ 1) for some hours. This resistance to hydrolysis means that the copolymer can be treated in an autoclave with saturated steam at 120° for various hours without loss of weight or detectable reduction in the molecular weight.

The formaldehyde–dimethylketene copolymer is less stable than the cyclic trioxane-ethers copolymers towards alkaline hydrolysis; in the latter type of copolymer, easily degradable functional groups are absent. The stability of the copolymer containing DMK is higher than that of polyoxymethylenediacetate having the same inherent viscosity; heating alkaline aqueous suspensions (0·1M Na_2CO_3) to 100° for two hours, caused weight losses of 50 per cent for the acetylated homopolymer and of 10 per cent for the copolymer with dimethylketene.

Physical and mechanical properties

The formaldehyde copolymers having a low DMK content (2–5 per cent) are soluble in dimethylformamide, in *p*-chlorophenol and in other liquids which are solvents for polyoxymethylene. Increasing the ketene content causes a change in the properties of the polymer: for example, if the dimethylketene content exceeds 15 per cent, the polymer is partially soluble in benzene and in chloroform.

It is known that processing (drawing and injection moulding) of the acetalic homopolymers presents two difficulties:

(1) Particular care in moulding[16] is needed for unstabilized materials because of the small difference between the m.p. (180°) and the temperature at which degradation starts (about 200°).

(2) Special thermal treatment is required after moulding[17] because of the low elasticity of the molten polymer and of the high crystallization rate.

The reduction in melting temperature (165–170° instead of 175–180°), obtained by using a formaldehyde copolymer, is a considerable technological advantage; the substance can be processed over a wider range of temperature. The reduction in the m.p. does not impair the thermal stability of the product. Another advantage of the formaldehyde–dimethylketene copolymer results from its wider melting range, the material becoming plastic before it melts completely.

The crystallization rate of the copolymer having a DMK content of 4·0 per cent is still very high; this is clearly shown by the fact that the relative crystallinity is about 70 per cent, after rapid quenching or after long annealing. The main physical-mechanical properties of the formaldehyde–dimethylketene copolymer and of other polyoxy-methylenic polymers are shown in Table 3. The properties of the product obtained by

TABLE 3. PHYSICAL-MECHANICAL PROPERTIES OF COMPRESSION MOULDED FORMALDEHYDE POLYMERS

	ASTM method	Unit	Acetylated homopolymer	Formaldehyde–DMK copolymer	Trioxane–ethylenoxide copolymer	
% of comonomer	—	—	—	4	2–3	
Inherent viscosity		—	0·60	0·62	0·6	
X-ray crystallinity		% vel.	80	70	75	
Melting temperature		°C	175	167	168	
Flexural strength	D790	Kg/cm²	1100	900	820	(a)
Flexural modulus of elasticity	,,	,,	32,000	22,000–23,000	25,000	
Impact strength	D256	cm Kg/cm	6·5–7·0	4·5–6·5	6	
Hardness Rockwell	D785	R scale	120–125	118	100	
Heat distortion temp.		°C	110±10	100–110	110	

(a) Literature data.

us are very similar to those of the trioxane–cyclic ether copolymer. It is confirmed that the presence of other monomeric units in the polyoxymethylenic chains affects the mechanical properties of the polymer (flexural and tensile strengths, Izod resilience). The changes are proportional to the dimethylketene content. If the moulding techniques and the thermal treatments are the suitable ones, the differences between the properties of the homopolymer and the copolymer containing 4 per cent DMK, are not large.

The heat distortion temperatures of the copolymers cannot be defined exactly but for the copolymer containing 4 per cent of dimethylketene, it is higher than 100° (determined by the ASTM D 648 method under a stress of 18·5 kg/cm²). The heat distortion temperature depends markedly upon the degree of structural regularity and on the distribution of the molecular weights, and so it is only to be expected that a range of values would be obtained. The electrical and optical properties, and the resistance to abrasion and to solvents are similar for polyoxymethylenediacetate and the copolymer.

Conclusions

Anhydrous formaldehyde and dimethylketene copolymerize in the presence of catalysts of the Lewis base type. The properties of the products vary with the ketene content. The ketene reacts with an adjacent formaldehyde unit by opening of the carbon–carbon double bond, yielding an ester group (—(CH₃)₂C—COOCH₂—). A random distribution of the monomer units in the polymer chain is found in copolymers having a prevailingly polyoxymethylenic structure and containing between 3 and 5 per cent of dimethylketene.

After removal of a fraction unstable at 160° (about 10 per cent of the crude polymer), a thermally stable polymer having a prevailingly acetalic structure is obtained; in its thermal and mechanical properties, it closely resembles the acetylated homopolymer of formaldehyde (Delrin type of Dupont) and the trioxane-cyclic ether copolymer (Celcon type of American Celanese). It is found that:

(1) Its degradation rate at very high temperatures (above 220°) is intermediate between those of the acetylated homopolymer and the trioxane copolymer.

(2) Its stability to hydrolysis can be closely compared with that of other acetalic polymers; its stability to alkaline hydrolysis is somewhat lower than that of the cyclic ether–trioxane copolymer, but is higher than that of the acetylated homopolymer.

(3) Its mechanical properties are a little inferior to those of the homopolymer, but they can be compared to those of the trioxane-cyclic ether copolymers.

The formaldehyde–dimethylketene copolymers have advantages over polyoxymethylenediacetate, resulting from their improved thermal stability at high temperatures and to their processability at lower temperatures. These copolymers may be preferred to the trioxane–cyclic ethers because of the basic nature of the polymerization catalysts used; this reduces very considerably the problem of removing residual catalyst from the crude product. It must be noted also that the process reported by us does not require synthesis of trioxane as a polymerization intermediate.

Finally, we think that the results obtained are of particular industrial interest; dimethylketene can be obtained in high yield by pyrolysis of isobutyric anhydride and acid[18,19] and it seems to be cheap enough for use as comonomer in small proportions.

EXPERIMENTAL

Preparation of the polymer. Dimethylketene was prepared by pyrolysis of isobutyric anhydride.[19] Before use, it was distilled from a small amount of aluminum alkyl. Formaldehyde was obtained by pyrolysis of cyclohexylhemiformal and was purified by cooling the gaseous stream to −10°.

In a typical polymerization run, a 1000 ml reactor was used; it was equipped with a mechanical stirrer, two dropping funnels (one of which had a jacket cooled to −78°), an inlet and an outlet gas tube. Operating under inert atmosphere, anhydrous n-heptane (450 ml) was introduced in the reactor, and the solutions of dimethylketene (4 ml in 50 ml n-heptane) and of triphenylphosphine (30 mg in 50 ml n-heptane) were prepared in the dropping funnels.

After cooling the reactor to −10°, the feeding of gaseous formaldehyde (4 g/min) was started, simultaneously with the addition of the dimethylketene solution (15 ml) and of the catalyst solution (15 ml). The mixture became turbid rapidly and the polymer precipitated in a powdery state. At 1 min intervals, small portions of the ketene and catalyst solutions were added, the whole addition taking 15 min. The reaction was stopped by excess methanol, and the precipitated polymer filtered and washed at 50° with an aqueous-alcoholic ammonia solution (1 per cent of NH₃). After drying in air at 40°, 54 g of polymer were obtained.

Examination of the polymer. The samples examined by chemical and physical methods were obtained from the crude polymer by washing with hot methanol and by removing the unstable fraction (by heating under vacuum at 170–175° for 4 hr).

Examination of the IR spectrum. The sample to be examined by IR (double beam spectrophotometer with NaCl prism and 2 cm^{-1} resolution at 10 μ) was in the form of a film pressed at 160–165°. The —CH$_2$OH end groups and ester groups were determined, from the intensities of absorption bands at 3420 and 1738 cm^{-1} respectively, using films of 0·25 and 0·10 mm.

The inherent viscosity. $\dfrac{\ln \eta_{rel}}{c(gr/100\,ml)}$ was measured in DMF at 150° (using solutions containing 0·5 per cent by weight of polymer) with Bischoff-type viscometers.

Degradation constant. The experiment was performed using an Eyraud thermal balance at 222° under an atm of N$_2$, using 150 mg of polymer; measurements were stopped when the polymer had lost 20–30 per cent of its initial weight.

During most of the degradation, a first order kinetic law was obeyed and the formula—$dw/dt = Kw$ (14) was used. Stabilities in N$_2$ at 250° and in air at 220° were determined by means of the same balance.

Thermal analysis. M.p. were determined by the Leitz polarizing microscope with a heating rate less than 1°/min. The measurements of differential thermal analyses (DTA) were carried out on a 0·02 g sample, using the Leeds and Northrup automatic apparatus with a temp increase of 5° per min (this high rate accounts for the small differences between the melting temps found by microscopic examination and from the endothermal maxima of the DTA curves). The diagrams reported in Fig. 3 refer to the behaviour of the polymer on the first melting.

Physical mechanical measurements. The physical mechanical measurements were performed according to the ASTM methods specified in Table 3, on compression moulded specimens, which were 2·6–2·8 mm thick, and aged for at least 48 hr at room temp.

The material for the physical-mechanical runs was obtained from the crude product by treatment with a hot solution of NH$_3$ in an autoclave; the polymer then heated to 160–170° for some hr in the presence of stabilizers (less than 2 per cent).

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Résumé—Lors de la polymérisation de formaldéhyde et de dimethylcétène anhydre en présence de catalyseurs anioniques (c'est-à-dire P(C$_6$H$_5$)$_3$) on peut obtenir un copolymère à structure polyoxyméthylénique dominante, contenant des groupes esters du type

$$\begin{array}{c} H_3C \quad\; O \\ |\qquad\; \| \\ -C-C-O-CH_2- \\ | \\ H_3C \end{array}$$
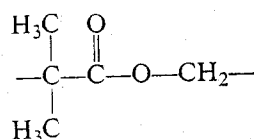
Ces groupes ont un effet considérable sur la stabilité thermique du polymère car elles empêchent le "dégrafage" des chaînes polyacétaliques.

Le comportement chimique et les propriétés physico-mécaniques d'un copolymère ayant une teneur de 4 pour cent en poids de diméthylcétène sont comparées avec ceux d'un homopolymère acétylé et d'un copolymère de trioxane–dioxolane.

Riassunto—Polimerizzando formaldeide anidra e dimetilchetene in presenza di catalizzatori anionici (p.e. P(C$_6$H$_5$)$_3$), è possibile ottenere un copolimero avente prevalente struttura poliossimetilenica e contenente gruppi esteri del tipo

$$\begin{array}{c} H_3C \quad O \\ | \quad\quad || \\ -C-C-O-CH_2- \\ | \\ H_3C \end{array}$$
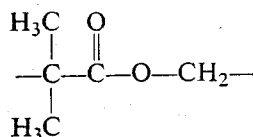
Questi gruppi hanno notevole influenza sulla stabilità termica del polimero poichè impediscono la completa degradazione delle catene poliacetaliche.

Il comportamento chimico e le caratteristiche fisico–meccaniche di un copolimero contenente dimetilchetene al 4 pro cento in peso vengono raffrontati con quelli dell'omopolimero acetilato e del copolimero triossano–diossolano.

Zusammenfassung—Durch Polymerisation wasserfreien Formaldehyds und Dimethylketen in Gegenwart von anionischen Katalysatoren (z.B. P(C$_6$H$_5$)$_3$), ist es möglich, ein Mischpolymerisat zu erhalten, welches vorwiegend von Polyoxymethylen-Struktur ist und Esterelemente des folgenden Typs enthält:

$$\begin{array}{c} H_3C \quad O \\ | \quad\quad || \\ -C-C-O-CH_2- \\ | \\ H_3C \end{array}$$
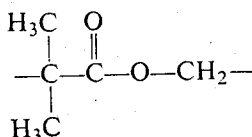
Diese Elemente haben eine erhebliche Wirkung auf die thermische Stabilität des Polymerisats, da sie die völlige Auflösung der Polyazetalketten verhindern.

Das chemische Verhalten und die mechanisch–physichen Eigenschaften eines Mischpolymerisats mit einem Inhalt von 4 Gewichtsprozent Dimethylketen werden mit denen des azetylierten Homopolymerisats und des Trioxan–Dioxolan–Mischpolymerisats verglichen.