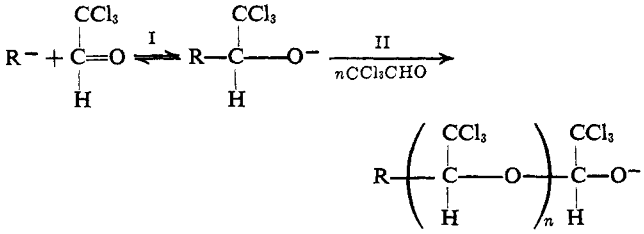
# Communications to the Editor

## Monomer-Cast Chloral Polymers

The polymerization of chloral, first reported by Liebig[1] in 1832, has been demonstrated to occur when initiated with anions or with certain acids.[2] Polychloral is ordinarily obtained as an intractable powder. Though plugs and thin films have been obtained[2c] and copolymers with substantial amounts of dichloroacetaldehyde have been cast into sheets,[2g] a general method for preparing objects of polychloral and chloral has not been available. It is our purpose here to describe a procedure that we have found effective for obtaining coherent chloral polymers in predetermined shapes. Our procedure is a monomer-casting process[3] involving a technique we call cryotachensic polymerization.[4]

In this process, initiation (I) and propagation (II) occur in two separate and distinct steps. In the first step, initiator is added to monomer that has been heated above the maximum temperature at which polymerization will occur. This temperature is about 58° for pure chloral and is reduced by addition of diluents. It is related to the ceiling temperature $T_c$ and is equal to $T_c$ for a 1 $M$ solution of monomer.



$$R^- + \underset{H}{\overset{CCl_3}{C}}{=}O \xrightleftharpoons{I} R{-}\underset{H}{\overset{CCl_3}{C}}{-}O^- \xrightarrow[nCCl_3CHO]{II} R{-}\left(\underset{H}{\overset{CCl_3}{C}}{-}O\right)_n{-}\underset{H}{\overset{CCl_3}{C}}{-}O^-$$

where R = nucleophile, *i.e.*, alkoxide = $^-O{-}C(CH_3)_3$. Above 58°, the homogeneous monomer–initiator mixture does not polymerize. The initiator may add to one monomer unit, but no propagation occurs. With lithium *tert*-butoxide and certain other initiators, the mixture can be held at 60° at least for several hours without deterioration. The mixture can be handled, poured, or transferred as long as the temperature remains above the maximum polymerization temperature. On the other hand, addition of initiator to pure chloral below the polymerization temperature causes immediate polymerization to noncoherent polymer in low yield.

In the second step, the mixture is cooled below the maximum polymerization temperature. Propagation begins immediately and polymerization proceeds as fast as the heat of polymerization can be removed. In the polymerization of thick sections the temperature within the sample remains at or above the maximum polymerization temperature, even with very efficient cooling, until heat can be dissipated through the surrounding first-formed polymer. This chloral polymerization is self-controlling. If the temperature within the polymerizing sample exceeds the maximum polymerization temperature, propagation stops until heat can be dissipated. If the initiated monomer is cooled under quiescent conditions, the polymer forms as a homogeneous gel which hardens as polymerization proceeds.

A wide range of nucleophiles is known to be effective as initiators for chloral polymerization.[2] Of those we have examined, all that are soluble in chloral or can be solubilized in chloral with nonprotic solvents are useful initiators in our monomer casting process. These include ammonium, phosphonium, and sulfonium halides or carboxylates, tertiary amines, and phosphines. Alkali metal and alkaline earth metal alkyls, alkoxides, carboxylates, and halides are also active initiators.

Copolymers of chloral with aliphatic[5a] and aromatic isocyanates[5] and with ketenes[6] can also be monomer cast to obtain coherent objects.[5a,6a] In our process aromatic isocyanates copolymerized most readily and gave products that have chloral/isocyanate ratios near those of the monomer charge.

We selected *p*-chlorophenyl isocyanate as the comonomer for most thorough study in our process. Sheets, films, or other objects of copolymers containing 2–10 mol % of *p*-chlorophenyl isocyanate are obtained in relatively high conversion, are clear, and are much improved in thermal stability as compared to homopolymer.

Both the homopolymer and the above copolymer show crystallinity by X-ray diffraction similar to the homopolymers of the literature.[2c,e] Both can be oriented at about 200°. Type of initiator, diluent, or the polymerization conditions used has no effect on polymer structure as indicated by infrared analysis or X-ray diffraction. Only one type of chloral chain, believed to have the isotactic configuration,[2c] has been observed.

These products are insoluble, infusible, and do not support combustion. They show no marked transition up to their thermal degradation temperature (about 200° for the copolymers) as judged by dsc or torsional pendulum measurements. At 180° copolymer samples retain 80% of their room-temperature tensile strength and tensile modulus. Most mechanical properties of chloral polymers are comparable to those of poly(methyl methacrylate). The thermal stability of the chloral–*p*-chlorophenyl isocyanate copolymer is similar to that of stabilized polyoxymethylene. Both homopolymer[2e] and copolymers are resistant to mineral acids and, although they may lose weight, they do retain mechanical properties after air oven aging.

A typical procedure for preparing coherent objects such as films, thick sheets, and castings involves heating highly purified chloral or a 95:5 chloral–*p*-chlorophenyl isocyanate mixture to 65° and adding to it 0.4 mol % of triphenylphosphine as a 1 $M$ solution in benzene. Since the polymerization is anionic, it is very sensitive to water and must be conducted in dry equipment and under dry nitrogen. Polymerization does

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(1) J. Liebig, *Ann. Chem.*, **1**, 209 (1832).

(2) (a) S. Gaertner, German Patent 165,984 (1905) and 170,534 (1906); (b) J. Boeseken and H. Schimmel, *Recl. Trav. Chim. Pays Bas*, **32**, 112 (1913); (c) A. Novak and E. Walley, *Trans. Faraday Soc.*, **55**, 1490 (1959); (d) J. Furukawa, T. Saegusa, and H. Fujii, *Makromol. Chem.*, **44–46**, 398 (1961); (e) I. Rosen, C. L. Strum, G. H. McCain, R. M. Wilhjelm, and D. E. Hudgin, *J. Polym. Sci., Part A*, **3**, 1535, 1545 (1965); (f) I. Rosen, *J. Macromol. Sci. Chem.*, **1**(2), 267 (1967); (g) G. H. McCain, D. E. Hudgin, and I. Rosen, *J. Polym. Sci., Part A-1*, **5**, 975 (1967).

(3) O. Vogl, U. S. Patent 3,454,527 (1969).

(4) The word *cryotachensic* is derived from Greek κρῦσς for cold, and τάχειντις for acceleration and means "acceleration upon cooling."

(5) (a) O. Vogl, French Patent 1,528,327 (1968); British Patent 1,151,002 (1969); U. S. Patent 3,668,184 (1972) to E. I. du Pont de Nemours and Co.; (b) H. Takida and K. Noro, *Kobunshi Kagaku*, **22**, 463 (1965); (c) M. C. Raes, J. V. Karabinos, and H. J. Dietrich, *J. Polym. Sci., Part A-1*, **6**, 1067 (1968); (d) Y. P. Getmanchuk, Y. L. Spirin, and R. I. Dryagileva, *Vysokomol. Soedin. A*, **10**, 139 (1968); (e) G. Odian and L. S. Hiraoka, *J. Polym. Sci., Part A-1*, **8**, 1309 (1970).

(6) (a) O. Vogl, French Patent 1,567,895 (1968); British Patent 1,151,003 (1969); U. S. Patent 3,668,184 (1972) to E. I. du Pont de Nemours and Co.; (b) Y. Yamashita and A. Uchikawa, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **71**, 758 (1968).

not occur because 65° is above the maximum polymerization temperature. The initiated mixture is promptly transferred to a warm mold having the shape of the object desired. Polymerization occurs immediately as soon as the temperature of the mixture in the filled mold falls below the maximum polymerization temperature. After 1 hr at 0° and overnight at room temperature, copolymer conversion is of the order of 80%. Homopolymer conversions are lower. Unreacted monomers are removed by extraction with acetone or methanol.

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## Quenching of Ketone Photodecomposition Reactions and Polymer Stabilization

It has frequently been suggested that the deactivation of excited carbonyl impurities by certain effective commercial stabilizers is an important mechanism for the stabilization of polyolefins against actinic degradation.[1–3] In particular, long-range (Förster) energy-transfer processes have been invoked.[1,3] However, the reported experimental evidence for quenching relevant to polyolefin stabilization either has involved ill-characterized chromophores in the solid polymer[1] (chromophores which are probably aromatic impurities rather than carbonyl substituents[4]) or has involved evidence obtained indirectly from model compound experiments in the liquid phase, such as anthracene triplet quenching[2] and inhibition of ketone-sensitized photooxidations.[5]

We have studied the photochemistry of two ketones (2-methyl-4-pentanone and 2,6-dimethyl-4-heptanone) which are structurally related to the macro ketones (a terminal methyl ketone and a backbone ketone) which are reported to be the carbonyl species involved in the initiation of photooxidative degradation of polypropylene.[6] The effects of various reported quenchers and related compounds on the photolyses of these ketones were examined in spectroscopically pure hydrocarbon solutions at 30°. Dilute solutions of each ketone (~0.05 *M*) were irradiated with the filtered light from a mercury lamp (wavelengths >310 nm) and the degradation products analyzed by glc. Short-path-length cells (0.1 cm) and relatively low additive concentrations (0.04–0.6 wt %, comparable to the concentrations used in practice to stabilize polyolefins) were employed so that the quenching effects even of those additives which absorbed significantly in the near uv or which produced absorbing products could be followed.[7]

The quantum yields for isobutane (the only observed alkane) and 2-methyl-4-pentanone production during the irradiation of 2,6-dimethyl-4-heptanone were found to be 0.50 ± 0.005 and 0.20 ± 0.03, respectively, in degassed, additive-free decahydronaphthalene. Quantum yields for carbon monoxide and propylene production agreed with the values for isobutane and the pentanone respectively, but were of a lower experimental accuracy. At the conversions employed (<5%) over 85% of the consumed ketone was accounted for by the Norrish type I products (CO and isobutane) and II products (olefin and pentanone). Neither 2-methyl-4-butanal nor 2,6-dimethyl-4-heptanol was detected; alcohol formation *via* intermolecular hydrogen abstraction from the solvent can be expected to be slow in comparison with the rapid intramolecular abstraction (the type II process).[8]

Several commercial polyolefin uv-stabilizing compounds[9] were found to be ineffective in quenching the formation of types I and II products in decahydronaphthalene or *tert*-butylbenzene. These included 2,6-di-*tert*-butyl-4-methylphenol, octadecyl 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenol)-

TABLE I
QUENCHING OF 2,6-DIMETHYL-4-HEPTANONE PHOTOLYSIS[a]

| Quencher | Quencher concn range, $M \times 10^3$ | Product $\tau k_q$ $M^{-1}$ [b] $i$-$C_4H_{10}$ | Product $\tau k_q$ $M^{-1}$ [b] 2-Methyl-4-pentanone |
|---|---|---|---|
| $O_2$ | 1.4–7.0 | | 140 ± 20 |
| *cis*-1,3-Pentadiene | 13–43 | >1000 | 70 ± 10 |
| Diphenylamine | 32–500 | 40 ± 4 | 110 ± 15 |
| 2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol) | 2.2–9.4 | 130 ± 13 | 130 ± 20 |
| 2,2′-Thiobis(4-*tert*-octylphenol) | 0.9–14 | 450 ± 50 | 110 ± 10 |
| Zinc dibutyldithiocarbamate | 1.0–7.0 | 280 ± 30 | 90 ± 10 |
| Zinc diisobutyl dithiophosphate | 1.6–6.4 | 550 ± 50 | ~0 |

[a] Osram SP 500 mercury lamp, Corning C.S. 1-64 filter. Decahydronaphthalene solutions, oxygen free unless otherwise specified. Initial ketone concentration 0.050 *M*, 0.1-cm path cells.
[b] Initial slope of the respective Stern–Volmer plots.

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(2) P. J. Briggs and J. F. McKellar, *J. Appl. Polym. Sci.*, **12,** 1825 (1968).

(3) J. E. Bonkowski, *Tex. Res. J.*, **39,** 243 (1969).

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(5) J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, **90,** 1001 (1968).

(6) D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2,** 587 (1969).

(7) The $I_a'$ value at a given wavelength in the presence of an absorbing additive was estimated from the observed total absorbance of each cell, the incident light intensity and the extinction coefficient at that wavelength, and the ketone concentration. These $I_a'$ values were then summed at 5-nm intervals across the effective ketone absorption spectrum (310 nm to 390 nm) to give the total absorbed intensity.

(8) G. Porter, R. W. Yip, J. M. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, **67,** 3149 (1971).

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