671. *Metal Ketyls as Initiators of Polymerisation of Vinyl Monomers. Polymerisation of Acrylonitrile and Methyl Methacrylate by Monosodium Benzophenone.**

By Albert Zilkha, Pedatsur Neta, and Max Frankel.

The polymerisation of acrylonitrile and methyl methacrylate by monosodium benzophenone in tetrahydrofuran has been investigated, in particular the effects of concentration of catalyst, monomer, added benzophenone, and temperature. The mechanism of the polymerisation is discussed.

Metal ketyls (the products of reaction of metals with ketones having no α-hydrogen atom) are radical anions in equilibrium with dimeric structures and act as catalysts for the polymerisation of vinylic monomers. We have studied the polymerisation of acrylonitrile and methyl methacrylate by monosodium benzophenone in tetrahydrofuran. The polymerisation of these monomers by sodium benzophenone has been reported recently by Smith;[1] some of his experiments were carried out with an excess of sodium, leading to formation of disodium benzophenone; moreover, the nature of the initiation by the catalyst was not known to him. In another preliminary study[2] an excess of benzophenone was used, which might interact with the growing polymer chains.

The polymerisation of acrylonitrile and of methyl methacrylate in tetrahydrofuran, in which the monomers are soluble even at low temperature, was investigated by us.

Results

The dependence of yield and molecular weight of polyacrylonitrile and of poly(methyl methacrylate) on the catalyst was studied. Experiments were carried out with identical quantities and concentrations of monomers, the monomer being added with stirring in one portion to the monosodium benzophenone prepared in tetrahydrofuran. With acrylonitrile (Table 1) the yield increased with increasing amounts of catalyst to approximately quantitative values. The molecular weights obtained (about 5500) did not depend on the amount of catalyst. With methyl methacrylate (Table 2) the yield was approximately quantitative even with lower catalyst concentrations, and the molecular weight increased with decrease in amount of catalyst, especially at the lowest concentrations used. At the higher concentrations of catalyst the decrease in molecular weight was very small. The molecular weights here were higher than for polyacrylonitrile.

Table 1. *Polymerisation of acrylonitrile. Dependence of yield and molecular weight on amount of catalyst.*

Acrylonitrile (10 ml.; 2·51 moles/l.) was added in one portion to monosodium benzophenone prepared in tetrahydrofuran (50 ml.). Polymerisation temp. 0°; time 1 hr.

Catalyst (mmole)	2·5	5	6·3	25
[Catalyst] (mole/l.)	0·0416	0·083	0·105	0·416
Polymer (g.)	3·5	4·5	7	8
Yield (%)	44	56	87	100
[η] (dl./g.)	0·155	0·145	0·15	0·155
$10^{-3}M$ *	5·8	5·3	5·6	5·8

* Average molecular weights of the polymers were calculated from intrinsic viscosities measured in dimethylformamide at 30° by use of the equation $[\eta] = 2{\cdot}33 \times 10^{-4}M^{0{\cdot}75}$ (Cleland and Stockmayer, *J. Polymer Sci.*, 1955, **17**, 473).

The dependence of yield and molecular weight on the concentration of monomers was studied under otherwise constant conditions. With acrylonitrile (Table 3) the yield decreased with increased concentration; the molecular weight was independent of concentration of monomer.

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* For a preliminary account of some of this work, see *Proc. Chem. Soc.*, 1959, 364.

[1] Smith, *J. Polymer Sci.*, 1959, **38**, 259.

[2] Inoue, Isuruta, and Furukawa, *Makromol. Chem.*, 1959, **36**, 778.

TABLE 2. *Polymerisation of methyl methacrylate. Dependence of yield and molecular weight on amount of catalyst.*

Methyl methacrylate (20 ml.; 2·67 moles/l.) was added in one portion to monosodium benzophenone prepared in tetrahydrofuran (50 ml.). Polymerisation temp. 0°; time 1 hr.

Catalyst (mmole)	6·3	13	25	50
[Catalyst] (mole/l.)	0·09	0·185	0·36	0·71
Polymer (g.)	17	18·5	18·5	18·5
Yield (%)	90	100	100	100
[η] (dl./g.)	0·15	0·13	0·11	0·105
$10^{-3}M$ *	50·5	41·2	32·6	30·6

* Average molecular weights of the polymers were calculated from intrinsic viscosities, measured in toluene at 30°, by use of the equation $[\eta] = 6{\cdot}87 \times 10^{-5}M^{0{\cdot}71}$ (Riddle, " Monomeric Acrylic Esters," Reinhold, New York, 1954, p. 64).

TABLE 3. *Polymerisation of acrylonitrile. Dependence of yield and molecular weight on amount of monomer.*

Acrylonitrile was added in one portion to monosodium benzophenone (6·3 mmoles; 0·09 mole/l.) prepared in tetrahydrofuran. The total volume of solvent and monomer was kept constant (70 ml.). Polymerisation temp. 0°; time 1 hr.

Monomer (ml.)	5	10	20
[Monomer] (mole/l.)	1·08	2·16	4·32
Polymer (g.)	3·5	7	10
Yield (%)	84	88	62
[η] (dl./g.)	0·145	0·15	0·145
$10^{-3}M$	5·3	5·6	5·3

TABLE 4. *Polymerisation of methyl methacrylate. Dependence of yield and molecular weight on amount of monomer.*

Methyl methacrylate was added in one portion to monosodium benzophenone (25 mmoles; 0·36 mole/l.) prepared in tetrahydrofuran. The total volume of solvent and monomer was kept constant (70 ml.). Polymerisation temp. 0°; time 1 hr.

Monomer (ml.)	5	10	15	20	30
[Monomer] (mole/l.)	0·667	1·33	2·0	2·67	4·0
Polymer (g.)	2·5	7	12·5	18·5	28·0
Yield (%)	53	75	89	100	100
[η] (dl./g.)	0·055	0·07	0·093	0·11	0·13
$10^{-3}M$	12·3	17·2	25·7	32·6	41·2

TABLE 5. *Polymerisation of acrylonitrile. Dependence of yield and molecular weight on polymerisation temperature.*

Acrylonitrile (10 ml.; 2·51 moles/l.) was added in one portion to monosodium benzophenone (6·3 mmoles; 0·105 mole/l.) prepared in tetrahydrofuran (50 ml.). Polymerisation time 1 hr., temp. as stated.

Temperature	−65°	−40°	0°	40°
Polymer (g.)	7	7	7	4
Yield (%)	87	87	87	50
[η] (dl./g.)	0·375	0·24	0·15	0·115
$10^{-3}M$	18·9	10·4	5·6	3·9

In the case of methyl methacrylate (Table 4) yield was quantitative with high concentrations of monomer, and the molecular weight increased with concentration of monomer.

The effect of temperature on the polymerisation was investigated between about −65° and +40°. With acrylonitrile (Table 5) the yield was the same for the temperature range −65° to 0°, decreasing at the higher temperature. Molecular weights of the polymers obtained at lower temperature were much higher owing to the decreased effect of chain transfer. A semi-logarithmic plot of molecular weight against the reciprocal of the polymerisation temperature gave a straight line, whose slope [3] corresponds to the difference in activation energy between propagation and termination of 2 kcal./mole, as calculated from the equation $\mathrm{d}\ln M/\mathrm{d}T = \Delta E/\boldsymbol{R}T^2$. Unlike the more reactive acrylonitrile, methyl methacrylate does not polymerise

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[3] Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, New York, 1953, p. 218.

significantly below −40° (Table 6). The yield was an optimum between −30° to 0°. Molecular weights decreased with increase in temperature.

TABLE 6. *Polymerisation of methyl methacrylate. Dependence of yield and molecular weight on temperature.*

Methyl methacrylate (20 ml.; 2·67 moles/l.) was added in one portion to monosodium benzophenone (25 mmoles; 0·36 mole/l.) prepared in tetrahydrofuran (50 ml.). Polymerisation time 1 hr., temp. as stated.

Temperature	−70°	−50°	−30°	−20°	−10°	0°	10°	20°	40°
Polymer (g.)	Trace	Trace	15	15	16	18·5	14	10·5	3·5
Yield (%)	—	—	80	80	86	100	75	56	19
$[\eta]$ (dl./g.)	—	—	0·135	—	0·125	0·11	0·094	0·083	0·071
$10^{-3}M$	—	—	43·5	—	39	32·6	26	22	17·5

TABLE 7. *Polymerisation of acrylonitrile in the presence of added benzophenone.*

Benzophenone was added with stirring to monosodium benzophenone (6·3 mmoles; 0·105 mole/l.) prepared in tetrahydrofuran (50 ml.), followed by acrylonitrile (10 ml.; 2·51 moles/l.). Polymerisation temp. 0°, time 1 hr.

Benzophenone added (g.)	0	10	20
[Benzophenone] added (mole/l.)	0	0·916	1·83
Polymer (g.)	7	7·5	7·5
Yield (%)	87	94	94
$[\eta]$ (dl./g.)	0·15	0·125	0·095
$10^{-3}M$	5·6	4·4	3

TABLE 8. *Polymerisation of methyl methacrylate in the presence of benzophenone.*

Benzophenone was added with stirring to monosodium benzophenone (25 mmoles; 0·36 mole/l.) prepared in tetrahydrofuran (50 ml.), followed by methyl methacrylate (20 ml.; 2·67 moles/l.). Polymerisation temp. 0°, time 1 hr.

Benzophenone added (g.)	0	5·5	15·5
[Benzophenone] added (mole/l.)	0	0·431	1·22
Polymer (g.)	18·5	12	7·5
Yield (%)	100	64	40
$[\eta]$ (dl./g.)	0·11	0·13	0·2
$10^{-3}M$	32·6	41·2	76

The effect, on the molecular weight, of addition of benzophenone to the monosodium benzophenone was investigated. With acrylonitrile (Table 7), the molecular weight decreased with increasing concentration of added benzophenone, while with methyl methacrylate (Table 8) the yield decreased with added benzophenone and the molecular weight of the unfractionated polymers increased.

Some insight into the degree of dispersion of the poly(methyl methacrylates) was obtained from the results of rough fractionation of two typical samples of poly(methyl methacrylate) (Table 9), one prepared in the presence of sodium benzophenone alone (*A*) and the other in the presence of added benzophenone (*B*) (1·22 moles/l.). Polymer *B* was much more dispersed. Besides having the typical fractions of *A*, polymer *B* contained additional fractions of very high molecular weight. The general dispersion of molecular weight of polymer *A* was not wide.

TABLE 9. *Fractionation of poly(methyl methacrylate).*

Polymer was dissolved in hot toluene (150 ml.) and fractionally precipitated with methanol.

A. Polymer (9 g.) (*M*,32,600) prepared as stated in Table 5 with 25 mmoles of catalyst.

Fraction	1	2	3	4
Wt. of fraction (g.)	2·5	2·5	2	2
$[\eta]$ (dl./g.)	0·12	0·115	0·095	0·09
$10^{-3}M$	36·9	34·7	27·1	24·6

B. Polymer (6 g.) (*M*,76,000) prepared as stated in Table 8 with 15·5 g. of added benzophenone.

Fraction	1	2	3	4	5
Wt. of fraction (g.)	0·7	1·5	1	1	1·5
$[\eta]$ (dl./g.)	0·63	0·135	0·125	0·11	0·1
$10^{-3}M$	381	43·5	39	32·6	28·5

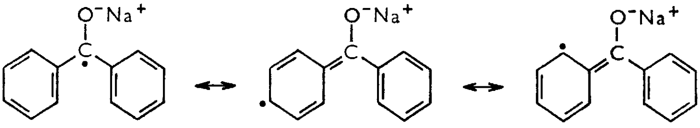
X-Ray diffraction diagrams of samples of the poly(methyl methacrylates) and of the polyacrylonitriles showed no crystallinity, the former even after swelling in toluene, ether, or methanol.

Discussion

Initiation.—Monosodium benzophenone is believed to be an equilibrium mixture between monomeric and dimeric structures:[4]

$$2\mathrm{Ph{\cdot}\dot{C}{-}\overset{+\,-}{O}Na} \rightleftharpoons \begin{array}{l}\mathrm{Ph_2C{\cdot}O^-Na^+}\\ \quad|\\ \mathrm{Ph_2C{\cdot}O^-Na^+}\end{array}$$

For the monomeric ketyl, seven resonating structures are possible, *e.g.*:



The possibility that the unpaired electron is on the oxygen atom and the anion on the carbon atom is ruled out on energy grounds.[5]

It follows that initiation may be by the free radical, by the anion (which is an alkoxide), or by both, or by the dianion of the dimeric structure. Polymerisation by the alkoxide part will give structure (I), a radical and a propagating anion; during the polymerisation two radicals may unite to give the benzopinacol structure (II). This, if free, may initiate an anionic polymerisation. The total result would then equal initiation through the dimeric structure.

$$\text{(I)}\ \cdot\mathrm{CPh_2{\cdot}O{\cdot}CH_2{\cdot}\bar{C}XR} \qquad {}^-\mathrm{O{\cdot}CPh_2{\cdot}CPh_2{\cdot}O{\cdot}CH_2{\cdot}\bar{C}XR}\ \text{(II)}$$

The initiation step in the polymerisation of acrylonitrile and of methyl methacrylate by monosodium benzophenone is through the alkoxide anion, as is substantiated by the following evidence: (*a*) Infrared spectra of our polyacrylonitriles and the poly(methyl methacrylates) showed absorption bands at 14—14·1 and 13—13·2 (monosubstituted benzene), as well as at 9—9·3 μ (dialkyl ether). The infrared spectra were identical in these features with that of acrylonitrile polymerised by sodium benzyl oxide.[6] (*b*) A copolymerisation experiment carried out under the conditions of Table 1, with acrylonitrile (10 ml.) and styrene (10 ml.), stopped after 3 min., gave 5 g. of polymer whose nitrogen analysis showed it to be pure polyacrylonitrile. Now the reactivity of styrene in radical polymerisation is greater than that of acrylonitrile,[7] while in anionic polymerisation it is very much lower. Therefore, the polymerisation is initiated anionically. (*c*) The reactivity of acrylonitrile is greater than that of methyl methacrylate; this is compatible with anionic polymerisation. (*d*) Polymerisation was effective even at −65° for acrylonitrile and at −30° for methyl methacrylate.

Further evidence for the initiation was obtained from the depolymerisation of a purified typical poly(methyl methacrylate) by heat; this gave benzophenone and diphenylmethanol besides monomer (see Experimental). The former two compounds can result from the decomposition of benzopinacol[8] groups present in the polymer. These findings

$$\mathrm{H{\cdot}[CMe(CO_2Me){\cdot}CH_2]_n{\cdot}O{\cdot}CPh_2{\cdot}CPh_2{\cdot}O{\cdot}[CH_2{\cdot}CMe(CO_2Me)]_m{\cdot}H} \longrightarrow \mathrm{COPh_2 + CHPh_2{\cdot}OH} + \text{Monomer}$$

also suggest that after initiation by alkoxide rapid dimerisation of the remaining free radicals of the ketyl occurs.

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[4] Wheland, " Advanced Organic Chemistry," Wiley, New York, 1949, 2nd edn., p. 719.

[5] Bent and Keevil, *J. Amer. Chem. Soc.*, 1936, **58**, 1367.

[6] Zilkha, Feit, and Frankel, *J.*, 1959, 928.

[7] Alfrey, Bohrer, and Mark, " Copolymerisation," Interscience Publ., Inc., New York, 1952, pp. 231—232.

[8] Thoerner and Zincke, *Ber.*, 1877, **10**, 1473; Valeur, *Bull. Soc. chim. France*, 1904, **31**, 1219.

Termination.—The mode of termination of the polymerisation of acrylonitrile may be understood from the annexed scheme.

Initiation $$\mathrm{C + M \xrightarrow{k_i} CM^-}$$

Propagation $$\mathrm{CM^- + M \xrightarrow{k_p} CMM^-}$$

Termination $$\mathrm{CM_n{}^- + M \xrightarrow{k_t} CM_nH + M^-}$$

The degree of polymerisation, assuming termination by chain transfer to the monomer:

$$\mathrm{P{\cdot}CH_2{\cdot}CH(CN)^- + CH_2{:}CH{\cdot}CN \longrightarrow P{\cdot}CH_2{\cdot}CH_2{\cdot}CN + CH_2{:}C(CN)^-}$$

is given by $k_p[\mathrm{M}][\mathrm{CM}_n]/k_t[\mathrm{M}][\mathrm{CM}_n] = \text{Constant}$. In accordance with this scheme we have shown that the molecular weight is independent of both catalyst and monomer concentrations and that the polyacrylonitriles contain terminal ($\mathrm{CH_2}$=) double bonds shown by infrared absorption bands at 5·9—6·1 μ; this is consistent with the assumption that termination is by chain transfer to monomer.

Methyl methacrylate, not possessing a reactive α-hydrogen atom, cannot have this mode of termination. This is indicated by the absence of infrared absorption bands at 5·9—6·1 μ for methylene double bonds. Further, the polymerisation mixture contained tetrahydrofuran, monomer, and monosodium benzophenone, none of which is able to donate a proton for termination of the anionic polymerisation.

In recent work [9] on the anionic polymerisation of methyl methacrylate it was suggested that termination can occur by the interaction of a growing anion with the ester group of the monomer or polymer, as in a Grignard reaction, with splitting off of a methoxide anion; no direct evidence was given, however, that such termination does occur during the polymerisation. The suggestion [10] that termination may proceed by shift of an ester group, leaving an unreactive carboxyl anion, has been contested on energy grounds.[11] However, recent work [11] of more exact nature on the anionic polymerisation of methyl methacrylate by anionic initiators has shown that self-termination, especially at low temperature, is negligible and that living polymers are obtained.

Acrylonitrile was added (see Experimental), at the end of the reaction, to the polymerisation mixture of methyl methacrylate after the consumption of catalyst (disappearance of the colour of the ketyl) and was polymerised to completion. The mixture obtained of poly(methyl methacrylate) and polyacrylonitrile yielded a small amount of a block polymer of acrylonitrile and methyl methacrylate containing 30—40% of acrylonitrile. Infrared spectra of the block polymers showed bands due to the nitrile group of the polyacrylonitrile at 4·4 μ and to methyl methacrylate at 5·8 μ.

This shows that carbanion propagation centres, still intact, of poly(methyl methacrylate) were present. The relatively small amount of block polymer and large amount of free polyacrylonitrile can be explained by the fact that most of the polymerisation of this monomer after initiation by some active centres of the poly(methyl methacrylate) occurred by chain transfer with monomer. This seems plausible as polymerisation would start more easily with an active monomer anion, obtained by chain transfer (see following scheme), than with a polymeric chain (the latter being also of a different character from the monomer).

$$\mathrm{P{\cdot}CH_2{\cdot}CMe(CO_2Me)^- + CH_2{:}CH{\cdot}CN \longrightarrow P{\cdot}CH_2{\cdot}CMe(CO_2Me){\cdot}CH_2{\cdot}CH(CN)^-\ (X)}$$

$$\mathrm{X + CH_2{:}CH{\cdot}CN \longrightarrow P{\cdot}CH_2{\cdot}CMe(CO_2Me){\cdot}CH_2{\cdot}CH_2{\cdot}CN + CH_2{:}C(CN)^-}$$

Termination by chain transfer

Active monomer anion

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[9] Schreiber, *Makromol. Chem.*, 1959, **36**, 86.

[10] Szwarc and Rembaum, *J. Polymer Sci.*, 1956, **22**, 189.

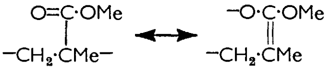
[11] Wenger, *Chem. and Ind.*, 1959, **35**, 1094.

Confirmation of this was that the free polyacrylonitrile obtained did not show infrared absorption bands at 13—13·2 and 14—14·1 μ (monosubstituted benzene) as does polyacrylonitrile formed by initiation with sodium benzophenone. It shows absorption at 5·9—6·1 μ for methylene double bonds.

Recent work [12] on the polymerisation of styrene by sodium naphthalene showed that the living polymers obtained were not sharply monodispersed and that the molecular weights at high concentrations of catalyst deviated very considerably from what should have been expected from Szwarc's equation: [13] D.P. $= [M]/\frac{1}{2}[C]$. This was explained by the fact that not all catalyst molecules start polymerisation and that the monomer adds more readily to a growing anion than to catalyst. In our case, it is quite possible that not all the catalyst molecules start polymerisation, for it is plausible that monomer adds more readily to a growing carbanion (which is much stronger than an alkoxide anion). Therefore, the molecular weight of the resulting polymers can be only slightly affected by increasing amounts of catalyst, especially at the higher concentrations, as found experimentally. It is also possible that the dispersion of molecular weight is not sharp, even if no termination exists. This is indicated by the fractionation.

At different temperatures there could be deviations in molecular weight depending on the reactivity of the alkoxide starting the polymerisation. It is expected that at higher temperatures more catalyst would participate in the initiation, lowering the molecular weight. Temperature may also affect the degree of dissociation of the ketyl between monomeric and dimeric structures which may have different activities as initiators. This fact also can partly account for the change in molecular weight.

Increase in molecular weight with concentration of monomer is possible if termination is absent or very slow. The living poly(methyl methacrylate) can also be stabilised by such resonating structures as:



$$\overset{O=C\cdot OMe}{\overset{|}{-CH_2\cdot CMe-}} \longleftrightarrow \overset{-O\cdot C\cdot OMe}{\overset{\|}{-CH_2\cdot CMe}}$$

These resonance-stabilising factors are of course much weaker than in the case of living polystyrene.[14]

Termination in the Presence of Added Benzophenone.—Benzophenone can add to the propagating anion to give an alkoxide:

$$P\cdot CH_2\cdot CXR^- + Ph_2CO \longrightarrow P\cdot CH_2\cdot CXR\cdot CPh_2\cdot O^-$$

This alkoxide which is weaker than a carbanion, is able to propagate additional polymerisation. In the case of the polymerisation of acrylonitrile, polymerisation may not be propagated by these alkoxides, owing to their relatively low concentration, the insolubility of the polymer formed, and the great possibilities of initiation from chain-transfer reactions with monomer. Thus benzophenone acts largely as terminator and its addition to the polymerisation mixture leads to a lowering of molecular weight, as was found.

It appears plausible that the reaction of the growing anion with benzophenone, similar to that of a Grignard reagent, is comparatively slow, especially at low temperature, so that " termination " does not occur at the same time on all the growing carbanions; thus, with methyl methacrylate the carbanions which were not " terminated " would increase greatly in molecular weight, because more monomer is available to them. This leads to a small fraction of the polymer's attaining very high molecular weight. This is supported by the results of the fractionation.

EXPERIMENTAL

Materials.—Nitrogen was freed from oxygen by passage through a quartz tube containing fresh copper wire at 600°, then through a 5% alkaline permanganate solution followed by a

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[12] Lyssy, *Helv. Chim. Acta*, 1959, **42**, 2245.

[13] Waack, Rembaum, Coombes, and Szwarc, *J. Amer. Chem. Soc.*, 1957, **79**, 2026.

[14] Frankel, Ottolenghi, Albeck, and Zilkha, *J.*, 1959, 3858.

20% solution of pyrogallol in 20% aqueous sodium hydroxide, and was dried by concentrated sulphuric acid. Tetrahydrofuran was dried over sodium hydroxide, refluxed over lithium wire, distilled, and boiled under nitrogen before use. Benzophenone (B.D.H.), m. p. 47—48°, was dried in a vacuum-desiccator. Acrylonitrile was purified (cf. Bamford and Jenkins[15]) by successive washings with 5% sulphuric acid, 5% aqueous sodium carbonate, and water. After being dried ($CaCl_2$), it was fractionally distilled at atmospheric pressure and stored in the dark over calcium chloride. Immediately before use, it was filtered and fractionally distilled *in vacuo* under nitrogen; the middle fraction, about 70%, was used. Methyl methacrylate was dried over sodium sulphate and before use was fractionally distilled under nitrogen at atmospheric pressure and then *in vacuo*; the middle fraction, about 70%, was used. Toluene was dried over sodium and distilled. Dimethylformamide was fractionally distilled.

Preparation of Monosodium Benzophenone.—The preparation of catalyst and the polymerisations were carried out under nitrogen. Into a three-necked flask fitted with a high-speed stirrer, a gas-adapter for introducing nitrogen, and a thermometer, tetrahydrofuran (50 ml.), sodium wire (1 equiv.; diam. 0·5 mm.) and benzophenone (1 mol.) were added, and the mixture was stirred. The blue colour of the ketyl appeared in a few minutes and the mixture was stirred for 15 min. thereafter. No residual sodium was found. The preparations were carried out on a 0·002—0·06 molar scale. Yield was determined by titration of filtered solutions. It was checked by the differential titration method,[16] the reaction with benzyl chloride being carried out for 30 min. at 40° (benzyl chloride reacts with the ketyl by the Williamson reaction to form ethers). Blank determinations were also carried out. Three trial checks on the yield gave 95 ± 5% when the above procedure was followed carefully.

Polymerisation of Monomers.—To the monosodium benzophenone prepared as described, dissolved in the required amount of tetrahydrofuran and cooled to the required temperature, cooled monomer was added in one portion with stirring. The temperature of the polymerisation was kept constant. The polymerisation was stopped after the required time by addition of 20 ml. of a 1 : 1 mixture of concentrated hydrochloric acid and methanol. Polyacrylonitrile was filtered off, washed with dilute hydrochloric acid, water, methanol, and ether (to remove benzophenone and monomer), and dried at 60°. Poly(methyl methacrylate) was precipitated from its solution in tetrahydrofuran by methanol. The polymer was usually precipitated in a sticky condition and was kept under methanol until it completely solidified. It was then filtered off, washed with methanol, dilute hydrochloric acid, water, and methanol, and dried in a vacuum-desiccator.

All polymerisation experiments were checked for reproducibility.

Polymer samples were further purified and dried for molecular-weight determinations. Viscosities of polymer solutions were measured in an Ostwald viscosimeter.

Depolymerisation of Poly(methyl methacrylate) by Heat.—Poly(methyl methacrylate) (10 g.), prepared as stated in Table 5 with 25 mmoles of catalyst, was triturated several times with hot methanol and filtered to ensure the complete absence of benzophenone. Evaporation of the methanol filtrate left no residue. The polymer was dried and then heated *in vacuo* at temperatures between 300° to 370° to effect depolymerisation. A colourless, and then a small quantity of a yellowish, liquid distilled. This mixed distillate was fractionated *in vacuo*. The main fraction was methyl methacrylate (refractive index). A second very small fraction had b. p. 155—175°/10 mm. (cf. benzophenone, diphenylmethanol); it gave a 2,4-dinitrophenylhydrazone, m. p. 238° (cf. the derivative of benzophenone; mixed m. p.). This fraction also gave a sensitive yellow colour reaction with concentrated sulphuric acid, as does diphenylmethanol but not benzophenone. In ethanol it showed maximum absorption at 252 mμ (benzophenone) and 214 mμ (diphenylmethanol).

Preparation of a Block Polymer of Methyl Methacrylate–Acrylonitrile.—Methyl methacrylate (20 ml.) was polymerised as stated in Table 5, with 6·3 mmoles of catalyst. After 2 hr. the polymerisation mixture was yellow (disappearance of ketyl). Acrylonitrile (10 ml.) was added and the reaction carried out for 10 min. 26 g. of polymer were obtained (~100%). Polymer (8 g.) was fractionated by consecutive extractions with boiling solvents (50 ml. each), as follows: three times with benzene, twice with acetone, twice with ethyl methyl ketone, once with dioxan, and once with chloroform. The benzene extract (5 g.) contained no nitrogen and was pure poly(methyl methacrylate). The acetone extract (0·5 g.) contained 8·7% of nitrogen,

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[15] Bamford and Jenkins, *Proc. Roy. Soc.*, 1953, *A*, **216**, 515.

[16] Williams, Van Den Berghe, Dunham, and Dulmage, *J. Amer. Chem. Soc.*, 1957, **79**, 1716.

showing it to consist of polyacrylonitrile 33% and poly(methyl methacrylate) 67%. The ethyl methyl ketone extract (0·1 g.) contained 9·8% of nitrogen, showing it to consist of polyacrylonitrile 37% and poly(methyl methacrylate) 63%. The dioxan and chloroform extracts contained no solute. The residue (2 g.) contained 25·3% of nitrogen, corresponding to approximately pure polyacrylonitrile. Infrared spectra of the block polymers showed the absorptions of both polyacrylonitrile and poly(methyl methacrylate).

DEPARTMENT OF ORGANIC CHEMISTRY, THE HEBREW UNIVERSITY,
JERUSALEM, ISRAEL.

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