Polymerization of Methyl Methacrylate by Organometallic Compounds. V. Dark Stoichiometric and Polymerization Reactions between Trialkylaluminums and Methyl Methacrylate

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SUMMARY

The stoichiometric reaction products of the reaction of triethylaluminum and methyl methacrylate (MMA) derive from a different complex to that responsible for the photosensitized, radical polymerization. The stoichiometric products are the result of nucleophilic attack on the carbonyl group of MMA (1,2 addition). No 3,4 nucleophilic adducts are found and it is questioned whether the one product usually believed to be the result of conjugate (1,4) attack does so arise. The reactions have been followed, in situ, using 60 MHz NMR and mechanisms are discussed. The nucleophilic addition reactions do not develop into an anionic polymerization chain. The equilibrium constants governing MMA-triethylaluminium complex formation are such that the 1:1 complex, the precursor of radical polymerization, prevails overwhelmingly in MMA-rich mixtures and the precursor of stoichiometric, nucleophilic, addition reactions prevails in Al-rich mixtures. The

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validity of diagnostic tests for polymerization mechanism based on the nature of concomitant, low molecular weight products is discussed.

It is confirmed that triethylaluminium does not initiate MMA polymerization in the dark over the temperatures 233-333°K. We find diisobutylaluminium hydride inert, in dark or light, at 298 and 333°K. Triisobutylaluminium only initiates MMA when illuminated at 298°K, but at 333°K there is also a significant dark rate. Preliminary copolymerization experiments, devised to elucidate the mechanism of this dark polymerization, suggest that, as in the case of the photo-sensitized, triethylaluminium-initiated, radical polymerization, it proceeds from a 1:1 MMA: trialkylaluminium complex.

In Part IV [1] we showed that the photo-initiated polymerizations of acrylate esters and acrylonitrile in the presence of triethylaluminium were free radical mechanisms. The initiation of methyl methacrylate (MMA) polymerization involved a photo-excited state of a 1:1 MMA:Et$_3$Al complex which forms in stoichiometric proportions once monomer is in excess.

At aluminium-rich reagent ratios rapid dark reactions occurred leading to several low-molecular-weight products, but no polymer. The nature of these products is of particular interest as the stoichiometric reactions between organometallic compounds and acrylate esters has sometimes been taken as evidence bearing on the mechanism of a concomitant polymerization reaction [2-4].

Triethyl aluminium does not initiate polymerization of MMA in the dark at any reagent ratio. This appears to settle previously conflicting reports. Minsker, Graevskii, and Razuvaez [5] report that while triethylaluminium was inactive (ambient illumination in their reaction vessels was no doubt low), triisobutylaluminium did initiate polymerization of MMA over the temperature range: 313-333°K. We confirm that, unlike triethylaluminium, triisobutylaluminium does initiate acrylate polymerization in the dark.
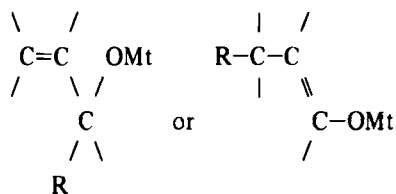
EXPERIMENTAL

Details of purification, manipulation, polymerization, and spectroscopic procedures are recorded elsewhere [1].

The low molecular weight products of the stoichiometric dark reactions were identified using mass spectrometry, gas chromatography, isotope labeling and NMR spectrometry. Details will appear in a forthcoming paper {6}.

RESULTS AND DISCUSSION

Stoichiometric Dark Reactions

Textbooks of organic chemistry (e.g., Ref. 7) classify the addition products of organometallic reagents and α,β-unsaturated carbonyl compounds as either 1,2 or carbonyl products or 1,4 or conjugate products depending on whether they derive from the intermediates (or putative intermediates):

```
   \   /                 |   /
    C=C    OMt         R—C—C
   /   \  /              |    \\
       C        or           C—OMt
      / \                    /
     R
```

I: 1,2 adduct   II: 1,4 adduct

Table 1 shows some of the products found among the hydrolyzed reaction mixtures of MMA with some typical reagents. On this classification, products like III and IV would be regarded as derivatives of I and V of II. It should be noted that the only "1,4 product" obtained has the methoxy group replaced by a second organic group from the reagent. No singlefold 1,4 adduct is found. If V is a 1,4 product, it can arise from the addition of a second molecule of reagent to II, as suggested by Owens, Myers, and Zimmerman [2], or by a methoxyl-alkyl exchange between II and reagent. This latter might well be intramolecular. The intermediates are probably associated or present in mixed associates with reagent, and the conformations of these associates are likely to bring Mt-R groups into favorable positions for intramolecular exchange. The twofold 1,2 adducts, IV, may similarly arise from alkyl-methoxy exchange or by a second 1,2-addition to the onefold adduct, III. The anionic polyvinyl chain and its hydrolyzed precursors VI are the result of successive 3,4-additions. While it has been suggested that 3,4 adducts only arise by rearrangement of 1,4 adducts, it is far more probable that these products are merely a function of the strong carbanionic character of II and its oligomeric and polymeric homologs, as originally suggested by Glusker [9]:

Table 1. Some of the Hydrolyzed Products of the Stoichiometric Addition Reactions of Methyl Methacrylate and Organometallic Reagents

	Reagent			
Product	Et Mg Br (Ref. 8)	Ph$_2$Mg, PhMgBr, BuMgBr, i-PrMgBr (Ref. 2)	n-BuLi (Ref. 3)	Et$_3$Al (this work)
III	—	None found	$\underset{\text{(trace)}}{\overset{\text{Me}}{\text{CH}_2\text{=C-C=O}}}\ \text{Bu}$	None found
IV	$\overset{\text{Me Et}}{\underset{\text{Et}}{\text{CH}_2\text{=C-C-OH}}}$	None found	$\overset{\text{Me Bu}}{\underset{\text{Bu}}{\text{CH}_2\text{=C-C-OH}}}$	$\overset{\text{Me Et}}{\underset{\text{Et}}{\text{CH}_2\text{=C-C-OH}}}$

V

—

$$\begin{array}{c} Me \\ | \\ PhCH_2-CH-C=O \\ | \\ Ph \end{array}$$
etc.

None found

$$\begin{array}{c} Me \\ | \\ EtCH_2-CH-C=O \\ | \\ Et \end{array}$$

VI

$$\begin{array}{c} Me \\ | \\ Et(CH_2-C)_n\,H \\ | \\ CO_2Me \end{array}$$
$$n = 2$$

$$\begin{array}{c} Me \\ | \\ Ph(CH_2-C)_n\,H \\ | \\ CO_2Me \end{array}$$
etc. $n = 1,2,3$

$$\begin{array}{c} Me \\ | \\ Bu(CH_2-C)_n\,H \\ | \\ CO_2Me \end{array}$$
$$n = 1,2$$

None found
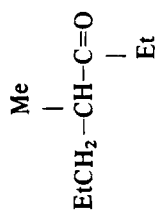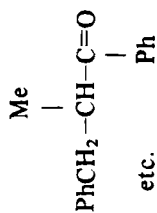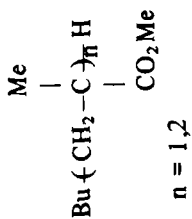
$$\text{\textasciitilde CH}_2-\overset{\displaystyle \overset{\text{Me}}{\big/}}{\underset{\underset{\underset{\displaystyle \text{MeO}}{\big/}}{\underset{\displaystyle \text{C}-\text{O}}{\big\|}}}{\text{C}}} \; \text{Mt}^{\oplus} \longleftrightarrow \text{\textasciitilde CH}_2-\overset{\displaystyle \overset{\text{Me}}{\big/}}{\underset{\underset{\underset{\displaystyle \text{MeO}}{\big/}}{\underset{\displaystyle \text{C}=\text{O}}{\big\backslash}}}{\text{C}^{\ominus}}} \; \text{Mt}^{\oplus} \qquad \textbf{VII}$$

For this reason **V** is sometimes regarded as a concomitant of anionic poly-merization while the 1,2 products are believed to he side products.

When MMA and triethylaluminium are mixed, complexes form rapidly and exothermically. When monomer is in excess (MMA:Al > 1) a yellow complex is formed which is stable at room temperature and below. Direct evidence of complex formation was manifest in the chemical shifts of the aluminium ethyl proto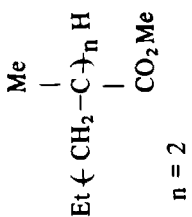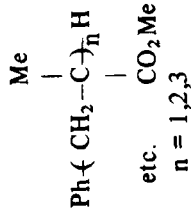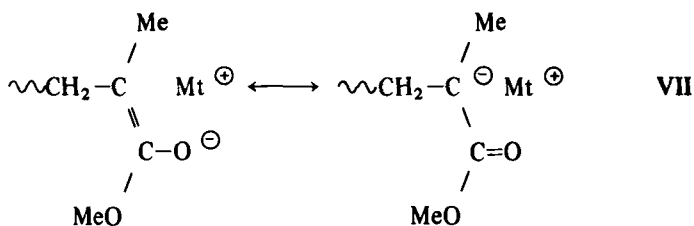ns in the NMR spectrum. The absence of any sig-nificant shift in the MMA vinyl protons relative to those of uncomplexed MMA indicated that this is a carbonyl complex and not a vinyl or con-jugate complex. The change of the internal chemical shift of the ethyl (methyl and methylene) protons with change of reagent ratio showed that the complex is 1:1 and strong. We believe it is a Wittig "-ät" complex: $CH_2:C(CH_3) \cdot C(OCH_3):O \rightarrow AlEt_3$ **(VIII)** . There is some evidence that it has charge-transfer character. **VIII** is responsible for the photo-initiated, radical polymerization when MMA-rich mixtures are exposed to visible and near-ultraviolet light. The chemistry of MMA-rich reaction mixtures is described in detail elsewhere [1]. It is relevant here to note that, apart from complex formation, there appears to be no further reaction in the absence of illumination.

At reagent ratios MMA:Al < 1, the complexes are short-lived and stoichiometric addition products are formed in the dark. At MMA:Al = 0.5, the normal yellow color obtained on mixing the reagents was followed by a sudden flash of red and sudden evolution of heat and then gradual fading of color. The reactions were carried out on a high-vacuum line at room temperature under the vapor pressure of the reagents. No increase in pres-sure was observed either on mixing the reagents or during their subsequent reaction. The internal chemical shift of the ethyl protons supported the evidence that a second complex was formed which probably has the stoichiometry Al_2Et_6,MMA. Irrespective of the evidence for the formation of a second complex, the reagent ratio is critical. When MMA:Al > 1.5 no stoichiometric products could be detected whether the mixture was illumi-nated or darkened. Between 1 > MMA:Al > 0.5 products were formed at

a rate which increased as the ratio decreased. When MMA:Al $\leqslant 0.5$, reaction was most rapid.
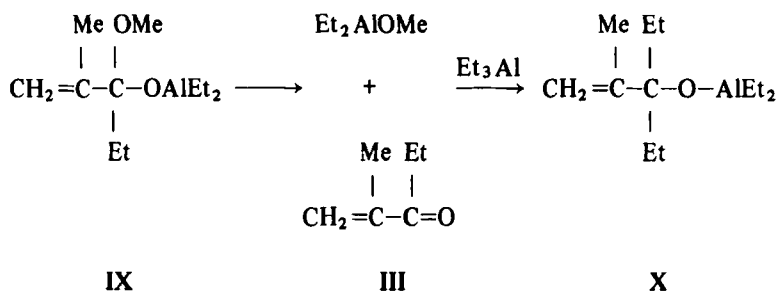
The main product found in hydrolyzed reaction mixtures was the twofold 1,2 adduct derivative: 2-methyl-3-ethyl-l-penten-3-ol (IV). It was accompanied by 4-methyl-3-heptanone (V) and two reduction products, 2-methyl-l-penten-3-ol and 2-methyl-2-propen-l-ol. A fifth, trace, product remains unidentified and, in long-term reactions, 2-methylpentanal was detected. Products of the type VI, e.g., 2-methylpentanoic acid methyl ester (n = 1) could not be detected.

The reaction was followed by 60 MHz NMR spectrometry and the importance of reagent ratio was again apparent. When MMA:Al = 0.29 no free nor complexed monomer was left by the time the first spectrum could be recorded (about 20 min from thawing the frozen reactants). The vinyl protons did not disappear, but, instead of the MMA doublet at 5.21 and 6.02 ppm, a singlet appeared at 4.8 ppm. (Tetramethylsilane resonance at 0.00 ppm.) This peak appears identical with the vinyl resonance in product IV. The species being observed cannot be the product IV which cannot arise until a hydrolyzing agent is added. We believe either the initial 1,2 adduct, $CH_2:C(CH_3)\cdot C(C_2H_5)(OCH_3)O$ Al Et_2 (IX), or the twofold adduct, $CH_2:C(CH_3)\cdot C(C_2H_5)O$ Al Et_2 (X), is responsible for this resonance. In either case the vinyl resonances would not be expected to differ significantly from that of IV. The vinyl resonance remained unchanged with time (18 days) although during this period changes occurred in the methoxy resonances which we have not yet been able to assign unambiguously. The integrated vinyl and methoxy proton resonances remained in the ratio 2:3 throughout, showing that saturation of the vinyl group was insignificant.

At reagent ratios between 0.5 < MMA:Al < 1 the reaction was sufficiently slow for the vinyl resonances of MMA (undoubtedly complexed) to be observed, as well as those of the alkenyloxyaluminiums (IX and/or X). The MMA peaks disappeared as the reaction progressed.

It seems likely that the mechanism of formation of the 1,2 adducts involves an MMA:Al_2Et_6 complex which rearranges rapidly to form the first adduct, IX. The alternative is a rapid bimolecular reaction between the MMA:$AlEt_3$ complex (VIII) and uncomplexed triethylaluminium. The NMR evidence for the existence of the MMA:Al_2Et_6 complex, while not entirely conclusive, leads us to prefer the first alternative. The likely hydrolysis product of the initial 1,2 adduct (IX) is III. This could not be detected even when the reaction mixture was hydrolyzed within 5 min of mixing. The absence of III in hydrolyzed reaction mixtures suggests that IX is rapidly converted to the twofold 1,2 adduct (X) (which hydrolyzes to IV; the main component in hydrolyzed reaction mixtures). One route for this is:

$$
\begin{array}{ccc}
\underset{|}{\text{Me}} \ \underset{|}{\text{OMe}} & \text{Et}_2\text{AlOMe} & \underset{|}{\text{Me}} \ \underset{|}{\text{Et}} \\
\text{CH}_2{=}\text{C–C–OAlEt}_2 \longrightarrow & + & \overset{\text{Et}_3\text{Al}}{\longrightarrow} \ \text{CH}_2{=}\text{C–C–O–AlEt}_2 \\
\underset{|}{} & & \underset{|}{} \\
\text{Et} & \underset{|}{\text{Me}} \ \underset{|}{\text{Et}} & \text{Et} \\
& \text{CH}_2{=}\text{C–C}{=}\text{O} & \\
\\
\textbf{IX} & \textbf{III} & \textbf{X}
\end{array}
$$

It has been pointed out that **IX** is likely to be complexed to an additional AlEt$_3$ moiety [10]. We find this suggestion attractive. There are several possible structures for this complex which make rapid intramolecular exchange of the methoxyl and an aluminium ethyl an attractive postulate, in which **IX** is converted to **X** without passing through **III** as an intermediate. We can find no evidence that any significant concentration of **III** develops in the reaction mixtures.

The mechanisms of polymerizations initiated by organometallic reagents are usually assumed to be analogous to those responsible for low molecular weight, side products. In fact the nature of the concomitant, low molecular weight products has sometimes been treated as a diagnostic test for polymerizaton mechanism. Clearly, such a criterion is invalid. In the present system the stoichiometric, nucleophilic, addition reactions are in no way associated with the polymerization which proceeds from a different complex and by a different mechanism. It seems that only low molecular weight products which can be, without ambiguity, attributed to a developing carbanionic polymerization chain can be taken as evidence that the polymerization is anionic. Only the oligomeric 3,4 adducts (**VI**) and the cyclic ketone:

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{Me} \quad \text{C} \quad \text{CO}_2\text{Me} \\
\diagdown \ \diagup \ \diagdown \ \diagup \\
\text{C} \quad \text{C} \\
\diagup | \quad \ | \diagdown \\
\text{R–CH}_2 \quad | \quad \ | \quad \text{Me} \\
\text{CH}_2 \ \text{CH}_2 \\
\diagdown \quad \diagup \\
\text{C} \\
\diagup \ \diagdown \\
\text{Me} \quad \text{CO}_2\text{Me} \\
\textbf{XI}
\end{array}
$$
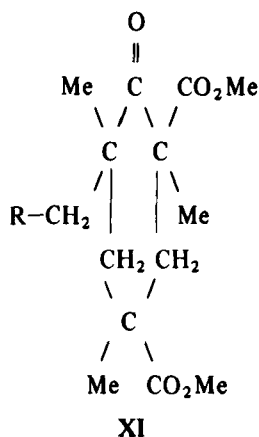
which is the product of an intramolecular cyclization-methoxide elimination of the trimeric MMA anion, fall into this classification. XI has been found in association with MMA polymerizations initiated by Grignard reagents [2] and diphenylaminodiethylaluminium or butylthiodiethylaluminium [11]. It is not found with triethylaluminium. V has also been assumed to be associated with the precursors of anionic chains, but we believe this is not the case. No onefold, 1,4 adduct precursor of V has been observed and no 3,4 adducts (VI) have been reported in which the methoxy has been exchanged for an alkyl group. It seems doubtful whether V is in fact a 1,4-addition product. It is most probably the result of vinyl attack on IX or a complexed form of III.

Polymerization Reactions in the Dark

Triisobutylaluminium forms yellow complexes with MMA which appear very similar to those formed by triethylaluminium. At 298°K the complex prevailing when MMA is in excess appears to behave very similarly to its ethyl analog in that polymerizatons only occur in the presence of light. At 333°K, however, polymerization also occurred in the dark, confirming the report of Minsker [5] that triisobutylaluminium is an active initiator at this temperature while triethylaluminium is not, though we must qualify the latter statement with the proviso, "in the absence of light."

Diisobutylaluminium hydride is often present as an impurity in triisobutylaluminium and is found in increasing equilibrium proportions as the temperature increases. Aluminium hydride groups are known to undergo rapid addition with a number of unsaturated substances [12]. In order to check whether the true initiator was in fact adventitious diisobutylaluminium hydride, we prepared this substance by pyrolyzing triisobutylaluminium at 413°K in a high-vacuum apparatus until the stoichiometric amount of isobutylene had been collected. Diisobutylaluminium hydride did not appear to complex with MMA. There was no noticeable evolution of heat and no color. Furthermore, we were unable to confirm previous reports [13] that diisobutylaluminium hydride initiated MMA polymerization. In our experiments, which were conducted at 333°K in sealed dilatometers with reagents triply-outgassed and distilled on a high-vacuum line, we could observe no polymerization in either light or dark. It seems that both the dark and photo-initiated polymerizations observed with triisobutylaluminium are associated with the yellow complex formed between this substance and MMA. In the case of diisobutylaluminium hydride, the hydride-bridged

structure of this trimeric species [12] is presumably too stable to permit the formation of diisobutylaluminium-MMA complexes.

Some preliminary experiments on MMA-styrene copolymerization have confirmed the general similarity of mechanism between the dark polymerization initiated by triisobutylaluminium and the triethylaluminium photo-initiated polymerization. Copolymerization of equimolar mixtures of styrene and MMA by triisobutylaluminium has been observed by Wexler and Manson [13]. They report copolymer compositions, in various experiments, in the range 30-40% styrene. The conditions of illumination are difficult to assess; the vessels are described as brown bottles. The authors suspected that they were not observing a simple radical copolymerization. We can confirm this. We have investigated the system at 60° in the dark.

Details of preliminary copolymerization experiments are shown in Table 2. The results were strikingly similar to the photo-sensitized triethylaluminium-initiated copolymerization [1] in that polymer does not form unless MMA:Al > 1. In the first experiment in Table 2, as in the first triethylaluminium experiment recorded there, a brief contraction was observed, but it soon ceased even though the yellow color of the complexes persisted. No polymer could be isolated. It seems likely that the small initial contraction is due to stoichiometric reactions. These results confirm that, as in the case of the photo-sensitized, triethylaluminium systems, the true initiator of MMA polymerization and copolymerization is a 1:1 MMA:trialkylaluminium complex. It seems probable that the mechanism is also a free radical one.

The copolymer compositions obtained do not, however, correspond to those of a simple radical polymerization. In the second experiment in Table 2 the polymerization was terminated with methanol at a contraction equivalent to 5% conversion. The methanol-insoluble polymer collected and analyzed (we could isolate no methanol-soluble polymer) amounted to only 0.5% by weight of the initial monomer feed. The composition of this copolymer corresponded to those reported previously [13, 14], though it was most significantly deficient in styrene content for a simple radical copolymer formed from this monomer ratio. In the third experiment, terminated at 12% conversion, 10% of the monomer was recovered as polymer in two fractions: a methanol-insoluble polymer containing 91% styrene and a methanol-soluble polymer containing 14% styrene. This exceedingly broad distribution of composition is most surprising and is in sharp contrast to the results of Wexler and Manson who used acetonitrile to fractionate their copolymers (the molecular weights were much higher than ours) and found very little difference in composition between the

Table 2. Styrene-MMA Copolymerization Initiated by MMA-Trialkylaluminium Complexes

Reagent	Monomer concentrations (M)		Solvent	Temp. (°K)	Illum.	Polymer composition, % styrene
	MMA	Styrene				
0.56 M, i-Bu₃Al	0.30	2.1	Toluene	333	Dark	None formed
0.41 M, i-Bu₃Al	0.82	2.5	Toluene	333	Dark	30%
0.14 M, i-Bu₃Al	2.74	2.94	Toluene	333	Dark	72%
a i-Bu₃Al	Equimolar[a]		Various	103–298	?	30-40% [13]
0.76 M, Et₃Al	0.38	3.5	Toluene	247	Light	None formed [1]
0.18 M, Et₃Al	0.37	3.2	Toluene	247	Light	Not analyzed [1]
0.5 M, Et₃Al	2.5	2.5	Toluene	273	Light	39% [14]

[a]Concentrations are not specified. In other experiments, where the concentration of i-Bu₃Al is cited, it lay in the range 0.9-4.6%.

extract and residue when triisobutylaluminium was the initiator. Our experiments were terminated when ample concentrations of both monomers in the free state would have been available. It raises the question of whether there are two parallel mechanisms operating, though it is difficult to imagine what they could be: one highly specific for MMA and the other for styrene. Clearly there is no point speculating until some experimental points are resolved. Are the differences between our observations and those of Wexler and Manson the result of controlled differences in conditions (e.g., low or high reagent concentration, dark or ambient illumination) or uncontrolled factors such as purity (nitrogen atmosphere or tubes sealed under high-vacuum)?

CONCLUSIONS

The reactions of organometallic compounds with α,β-unsaturated compounds are manifold. In the case of acrylate esters and triethylaluminium, and probably also triisobutylaluminium, two classes of reaction, nucleophilic addition and radical addition, proceed from different complexes. The equilibrium constants governing these complexes have values such that the two mechanisms operate over mutually exclusive reagent ratios, and the reactivity factors are such that only the radical addition reaction develops into a polymerization chain. This raises the question whether complexes are involved in the reaction of other organometallic compounds with acrylate esters and, if they are, does a dual mechanism also apply? Interesting cases could arise. If reactivity factors were such that both mechanisms led to chain polymerization, then equilibrium constants such as we have in the triethylaluminium system would enable us to switch mechanisms from radical to anionic by adjusting reagent ratio. If the equilibrium positions were different, we would have parallel mechanisms. In cases where only one mechanism leads to a polymerization chain, the stoichiometric reaction products (other than those which are definitely side products of an oligomeric polymerization chain) are valueless as a diagnostic test for the polymerization mechanism. They are likely to be products of the other mechanism. We were exceedingly fortunate to have made our first study on a system where it was possible to separate the dual mechanisms by controlling the complex equilibrium.

ACKNOWLEDGMENTS

REFERENCES

[1] P. E. M. Allen and B. A. Casey, Preprints IUPAC, ISCM Congress, Budapest, 1969; *Eur. Polym. J.*, In press.

[2] F. H. Owens, W. L. Myers, and F. E. Zimmerman, *J. Org. Chem.*, **26**, 2288 (1961). W. E. Goode, F. H. Owens, and W. L. Myers, *J. Polym. Sci.*, **47**, 75 (1960).

[3] N. Kawabata and T. Tsuruta, *Makromol. Chem.*, **86**, 231 (1965).

[4] S. Murahashi, H. Yuki, K. Hataba, and T. Obokata, *Kobunshi Kagaku*, **24**, 30 (1967).

[5] K. S. Minsker, A. I. Graevskii, and G. A. Razuvaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 1483.

[6] P. E. M. Allen and B. A. Casey, To be published.

[7] T. Eicher, *The Chemistry of the Carbonyl Group* (S. Patai, ed.), Wiley (Interscience), New York, 1966, p. 621.

[8] A. I. Lebedeva and E. D. Vainrub, *Zh. Obshch. Khim.*, **22**, 1974 (1952); **24**, 1207 (1954); **26**, 2436 (1956).

[9] D. L. Glusker, E. Stiles, and B. Yoncaskie, *J. Polym. Sci.*, **49**, 297 (1961).

[10] T. Mole, Private communication.

[11] S. Murahashi, H. Yuki, K. Hataba, and T. Obokata, *Kobunshi Kagaku*, **24**, 309 (1967).

[12] See, e.g., R. Köster and P. Binger, *Advan. Inorg. Chem. Radiochem.*, **7**, 263 (1965).

[13] H. Wexler and J. A. Manson, *J. Polym. Sci., Part A*, **3**, 2093 (1965).

[14] P. E. M. Allen and B. A. Casey, *Eur. Polym. J.*, **2**, 9 (1966).