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Preliminary communication

Methynyltricobalt enneacarbonyl compounds
II*. Initiation of radical polymerization by $Co_3(CO)_9CY$ complexes

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Metal carbonyls are known to initiate radical polymerization. The initiator activity seems to be proportional to the number of metal atoms in the complex[2]. On the other hand comparison of the results obtained with $Co_2(CO)_8$ (practically inactive) and $Mo(CO)_6$ (rather active)[3] suggest that more stable complexes would show higher initiator activity. $Co_3(CO)_9CY$ (I) compounds, containing 3 metal atoms and showing outstanding stability*, would be expected as active initiators, in fact an earlier paper[3] reports initiator activity of a compound formulated as $Co_3(CO)_9H(PhC_2H)$** in polymerization of methyl methacrylate as comparable with that of $Mo(CO)_6$ or AZDN.

These considerations and the observation of Bamford *et al.*[3] prompted us to study the initiator activity of compounds (I) systematically.

The experiments were performed with 40–70 v/v % n-hexane solutions of the monomers, with or without various amounts CCl_4 at 25–70 °. The polymers precipitated from the n-hexane solution were monitored by IR spectroscopy, elemental analyses and viscosimetric mol.wt. determination. Before mol.wt. measurements the polymers were purified by repeated dissolution in DMF and reprecipitation with MeOH at 0 °. Measurements were performed with an Ubbelode Viscosimeter in DMF solution at 25 °.

The derivatives (I) exhibited different initiator activity depending on the structure of Y. This is qualitatively in accordance with investigations on the rate of CO ligand exchange[6] (the first step of the initiation process should be the loss of a CO ligand[2]) as well as with previous suggestions[7] concerning the character of the apical carbon atom in the carbide cluster (*i.e.* the partial sp^2 or sp character of this carbon should facilitate transmission of the electronic effects of Y to the CO ligands).

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* Bor *et al.*[4] report that $Co_3(CO)_9CCl$ could be stored under air for more than 3 years without any considerable change.
**This formula most probably corresponds to $Co_3(CO)_9CCH_2Ph$, *cf.* ref. 5.

In experiments with acrylonitrile monomer the order of the initiator activity was found to be Y = Cl ≃ H ≃ Br > Ph > F ≃ i-Pr ≃ C_2F_5*. Methyl acrylate did not polymerize significantly under similar conditions with (I) Y = H, i-Pr and C_2F_5 and polymer yields with Y = Br or Ph were comparable with those obtained from acrylonitrile with Y = C_2F_5. This behaviour is somewhat unexpected since the overall reaction rate coefficient of methyl acrylate in radical polymerization surpasses that of acrylonitrile. On the other hand, 1/1 v/v mixtures of acrylonitrile and methyl acrylate polymerized with (I) Y = Br, yielding copolymers which contain ~1/1 molar proportions of both monomer units. The derivatives (I) Y = H and Ph did not show appreciable activity in copolymerization.

The viscosimetric measurements indicate that the mean mol. wt. of the polymer also depends on the structure of Y in the compounds (I) used as initiators: the higher the initiator activity, the lower the mol. wt. of the product. Thus *e.g.* molecular weights of 1.96×10^5 and 4.80×10^5 were found for acrylonitrile polymers prepared under identical conditions in the presence of (I) Y = Cl and Ph derivatives respectively.

Polymerization of vinyl acetate, methyl methacrylate and 4-vinylpyridine was also attempted under similar conditions with (I) Y = Br as initiator. Methyl methacrylate and 4-vinylpyridine polymerized readily while vinyl acetate did not show detectable polymerization.

To sum up, the order of polymerization activity of the monomers investigated is 4-vinylpyridine ≫ methyl methacrylate > acryl nitrile ≃ acryl nitrile + methyl acrylate > methyl acrylate when (I) Y = Br is used as initiator.

In all cases 10^{-3}–10^{-2} molar concentrations of CCl_4 were necessary to achieve significant yields (1 to 100%) of the polymers. This indicates that the presence of chain transfer agent is needed also in the case of (I) Y = halogen compounds.

Our result can be compared with the recent observations of Elder and Robinson[8] who reported olefin derivatives of compounds (I) via CO substitution. Analogous complexation of the monomer may be one of the initial steps in the polymerization. Kinetic studies have been initiated to elucidate this interesting point.

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*This compound has not yet been reported. It was prepared from $CCl_3C_2F_5$ with $[Co(CO)_4]^-$ in THF. IR absorptions in the 1800–2200 cm^{-1} range were: (in n-hexane) 2114.0 w; 2071.5 vs; 2052.5 s; 2041.0 w ± 0.5 cm^{-1}, analyses and mol. wt. measurements were satisfactory. Details of preparation and spectra will be reported later.

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