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UV-induced cross-linking of polyvinylmethoxymethacrylamide films containing transition metal β-diketonates

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The photoinduced cross-linking of a solid polyvinylmethoxymethacrilamides containing transition metal chelates is accompanied by the formation of long-lived free radicals which can be detected directly up to 300 K.

β-Diketonates of transition metals are well known as initiators of the radical polymerization of unsaturated compounds.[1,2] In the case of the polymerization of vinyl monomers above 373 K, β-diketonates are the source of primary free radicals due to thermal decomposition of the chelate. The experimental study of free radical formation as a result of the thermal decomposition of metal chelates has been reported previously.[2,3]

The radical polymerization of unsaturated compounds in the presence of donor additives proceeds at 313–353 K. The mechanism of primary free radical generation by metal β-diketonate + donor additive complexes has not been apparent till now. Free radical formation in such molecular systems has been studied and proved indirectly.[4,5]

The polymerization of unsaturated compounds in the presence of transition metal β-diketonates is activated also by irradiation methods (photoinitiation, γ-radiation) and can proceed at temperatures under 300 K. The determination of the photoinduced polymerization mechanism within this temperature range is difficult because at least three reaction paths are possible in the system: radical polymerization,[1,2,6] ion polymerization,[1,2,7] cyclodimerization due to complex photoexitation.[7]

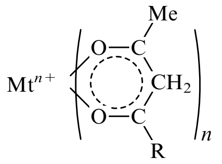
In the case of photoinduced polymer cross-linking in the presence of metal chelates one can suppose a radical mechanism of the reaction. Data on the formation of free radicals during $\mathrm{Co(acac)_3}$ photolysis in monomer solution[8] and $\mathrm{Mn(acac)_3 + C_2H_5OH}$ photolysis (77 K)[9] support this supposition. Data about free radical formation during UV irradiation of a polymer + transition metal β-diketonate system are absent from the literature.

We have studied the cross-linking under UV radiation of polyvinylmethoxymethacrylamide (PVMMA) containing metal-chelates. The metal-organic initiator of cross-linking was dissolved in an aqueous solution of PVMMA of the general formula:

$$\sim(\mathrm{CH_2{-}CH})_n\sim \qquad \mathrm{Me}$$
$$\mathrm{OCH_2N(H)C(O)C{=}CH_2}$$

where n = 1250, before casting onto a glass substrate.

Acetylacetonates (acac) of Cr^{3+}, Co^{3+}, Mn^{3+}, Ni^{2+} and ethylacetoacetate (eacac) of Cu^{2+} of the general formula:

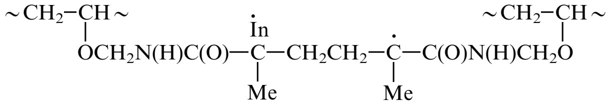


where Mt = metal ion and R = Me or OEt, were used as initiators. The irradiation was carried out by the unfiltered light of a high pressure mercury-quartz lamp (PRK-4).

As a result of UV irradiation the cross-linking of PVMMA occurs *via* unsaturated bonds. Their extent of conversion (%) depends on the time of exposure to a power of 0.5. Exposure of a PVMMA + $Co(acac)_3$ film for 5, 25 and 30 min leads to relative changes of transmission in the region of C = C bond vibrations (5, 12 and 14.3%, respectively). The gel-fraction amount in samples exposed for 3, 5 and 15 min consists of 53.0, 66.0 and 91.0% conversion, respectively.

UV irradiation of metal-chelate-free PVMMA films for more than 30 min does not lead to polymer cross-linking. The UV-exposed PVMMA samples were dissolved in boiling water. No changes occured in the 1640 cm^{-1} band intensity. The EPR signal in the $g = 2.00$ region was absent.

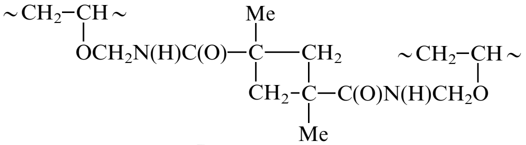
The molecular masses of the chains between the junction points in PVMMA have been estimated based on dynamic mechanic spectroscopy data for PVMMA + $Co(acac)_3$ samples exposed for 15 to 30 min using the relationship $M_c = 3RTd/E_\infty$,[10] where M_c is the mean molecular mass of a linking fragment in the polymer chain, d is the density of PVMMA, T is the temperature and E_∞ is the equilibrium shear modulus. This relationship is reliable for polymer networks with a high density of cross-links, as is the case in the PVMMA films studied. The obtained values at 2×10^2 agree with the molecular mass of the network fragment of the structure **A**:



$$\begin{array}{c}\sim CH_2-\underset{|}{C}H\sim \\ OCH_2N(H)C(O)\end{array}-\underset{Me}{\overset{\dot{In}}{C}}-CH_2CH_2-\underset{Me}{\overset{\bullet}{C}}-\begin{array}{c}\sim CH_2-\underset{|}{C}H\sim \\ C(O)N(H)CH_2O\end{array}$$

A

for the radical mechanism of cross-linking, or of structure **B:**



B

for the non-radical mechanism of [2 + 2] photocycloaddition.[7] In the latter case the quasiaromatic chelate rings of the metal compound may act like donor–acceptor chromophores[7] due to their donor–acceptor bonding with PVMMA unsaturated fragments.

It should be mentioned that the optical density of the absorption band with a maximum at 600 nm, characterizing the d–d transitions in the Co^{3+} ion, decreases in exposed PVMMA + $Co(acac)_3$ films. The exposure time was 3, 5 and 15 min. The band optical densities have the values of 0.91 for unexposed and 0.74, 0.56 and 0.53 for exposed films, respectively. This fact may be explained by initiator consumption during UV exposure due to free radical formation caused by photolysis of the metal chelate.

In the present study we have succeeded for the first time to register directly free radical formation in a polymer + metal chelate system under UV irradiation at the room temperature. The detection of free radicals was carried out without freezing the system. This was possible because in a solid PVMMA matrix the diffusion recombination of free radicals is limited and, therefore, the lifetime of the radicals grows significantly.

Free radical formation was revealed by using EPR for PVMMA films containing the paramagnetic $Cu(eacac)_2$ initiator. Figure 1 shows the structure of the EPR spectra of $Cu(eacac)_2$ in the PVMMA matrix before (*a*) and after 20 min of UV irradiation (*b*) and the EPR spectrum of the detected free radical (*c*).

The EPR spectrum of an unexposed PVMMA + $Cu(eacac)_2$ system shows an anisotropic structure (splitting of $\parallel$ and $\perp$ components) of the g-factor and also a superfine structure in the $g_\parallel$ region.The $g_\parallel$ and $A_\parallel$ parameters of $Cu(eacac)_2$ in a PVMMA matrix (2.320 and 167×10^{-4} cm^{-1}) and parameters of $Cu(eacac)_2$ in a frozen (77 K) chloroform–toluene matrix (2.276 and 187×10^{-4} cm^{-1}) have been compared. In the latter case the donor-acceptor interactions with the metal-chelate are negligible. The comparison shows that the PVMMA matrix forms donor-acceptor bonds with $Cu(eacac)_2$. The $g_\parallel$ and $A_\parallel$ parameters of films after UV irradiation changes and become 2.291 and 173×10^{-4} cm^{-1}, respectively. Taking into account their high sensitivity to ligand nature in copper(II) chelates[11] the conclusion can be made that the donor-acceptor bonding of $Cu(eacac)_2$ with the polymer matrix changes due to the cross-linking.

The EPR spectrum of an exposed PVMMA film keeps the main features of the unexposed film spectrum. However, an additional signal arises with a central component in the $g = 2.00$ region. Undoubtedly this signal corresponds to free radicals that have been formed due to irradiation of the PVMMA + $Cu(eacac)_2$ film. The signal possesses five well resolved components with g-factor and hyperfine interaction constant values equal to 2.00 and 23×10^{-4} cm^{-1}, respectively.

The free radical presence in the PVMMA + $Cu(eacac)_2$ system in combination with the regularities of cross-linking observed allow us to prefer the radical mechanism of cross-linking with formation of structure **A** for the network fragment.

In the PVMMA films studied the cross-linking process is initiated by the free radicals formed due to the UV irradiation of introduced metal chelates. In ref. 12 it is pointed out that metal chelate introduction may lead both to inhibition and to acceleration of the polymerization process. These phenomena

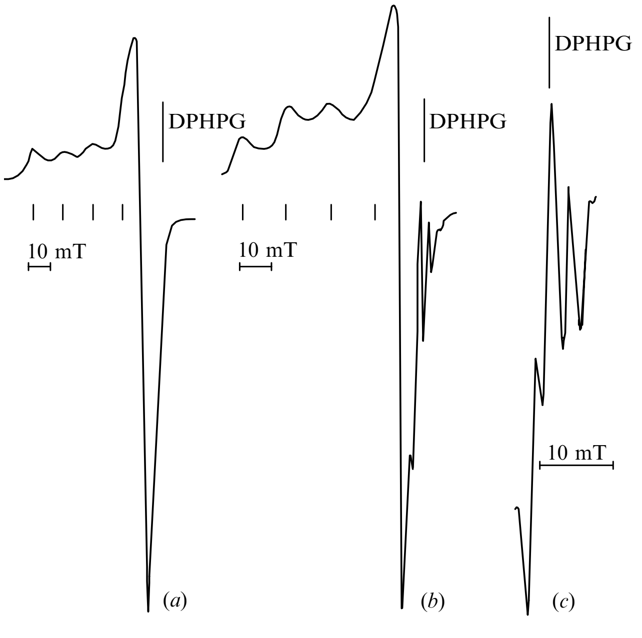


Figure 1 The EPR spectra of PVMMA + $Cu(eacac)_2$ films unexposed (*a*), UV exposed for 20 min (*b*) and the EPR spectrum of detected free radicals (*c*) at 300 K.

are characteristic of a polymerizing system which is able to form free radicals itself under UV irradiation. In such systems the metal chelate ligand free radical formation increases the probability of diffusion recombination with macroradicals, leading to polymerization process inhibition. Conversely, the accelerating effect of transition metal β-diketonates can be explained as a result of functional group activation due to their coordination by metal chelates.[13]

In the PVMMA samples under consideration the only source of primary free radicals is the chelate molecule photodegradation. It is difficult, therefore, to relate the EPR spectrum (*c*) to the initiator ligands or polymer fragment. Simultaneously, the direct detection of photoinduced free radical formation in polymer + metal chelate systems below 300 K is evident. This process was earlier only assumed to have been studied indirectly and in the presence of additives.[2,4,5] Furthermore, in our opinion the long lived free radicals detected in the polymer matrix at room temperature may stimulate the creation of a new approach in the study of radical processes in solids.

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