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Features of Network Formation in the Chain Crosslinking (Co)Polymerization

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Summary

Analysis of experimental results on the chain (co)polymerization of bisunsaturated monomers suggests that cyclization plays a decisive role already at the onset of the reaction. At medium and elevated concentrations of the bisunsaturated compound, compact microgel-like particles are formed, which give rise to a gel mainly by participating in the polymerization reaction only with pendant double bonds in their surface layer, and not with double bonds in the interior. This mechanism is reflected in an apparent decrease in reactivity of the pendant double bonds.

Introduction

Experimental experience gained in the recent decades shows that the process of network formation by the chain crosslinking (co)polymerization, particularly at its beginning, exhibits the greatest deviation from the course corresponding to the tree-like model of network formation (cf.e.g. STOCKMAYER 1943, FLORY 1953, GORDON and TEMPLE 1976). Analysis of experimental results has led to the predominant conclusion (cf.e.g. KAST and FUNKE 1979, DUŠEK 1979) that the cause of such special features lies in a strong cyclization with respect to the formation of intermolecular crosslinks. This general view has been lately questioned (OKASHA et al. 1979), and a view has been forwarded that at the beginning of the process intramolecular cycles do not play any major role and explanation of deviations is to be rather sought in a decreased reactivity of pendant double bonds. It has also been claimed that the copolymer structure has been never accurately related with the parameters of copolymerization and that the reactivity of pendant double bonds is generally ignored. In this study we try to reexamine both theoretical arguments and published experimental results, including some novel experimental data on the chain crosslinking

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(co)polymerization.

Logical reasonings show that the chain character of the polymerization process results in that at the very onset of (co)polymerization the monomer(s) contain so few growing macroradicals and terminated chains with pendant double bonds that the probability of an intermolecular reaction of the radical with the pendant double bond of another chain, α, is very small (zero in the limit of zero conversion), while the probability of an intramolecular reaction of the radical with pendant double bonds on the same chain, σ, is finite in this limit (Fig.1). These facts lead to high values of the concentration ratio of intra- and intermolecular crosslinks, σ/α, and to its divergence in the limit of zero conversion. A nonzero value of σ depends on the possibility of contacts between the radical and the double bond and the chemical reactivity of the pendant double bond. For divinyl monomers, the chemically-dependent reactivity of the pendant double bond may be weaker or stronger than, or close (e.g., for ethylene dimethacrylate) to the reactivity of double bonds in the monomer. The probability of the contact is given by chain flexibility and by steric hindrances (if any) in the neighbourhood of the reacting sites. The chain flexibility is usually sufficient for the formation of intramolecular links; for linear and weakly crosslinked chains, steric factors should play no important role. Hence, no general causes exist which would impede cyclization from predominating over the intermolecular reaction at the beginning of polymerization. Computer simulation of the polymerization of a divinyl monomer on a cubic lattice performed by us demonstrated strong cyclization, while indicating at the same time that a considerable part of pendant vinyls were not able to react because of steric reasons.

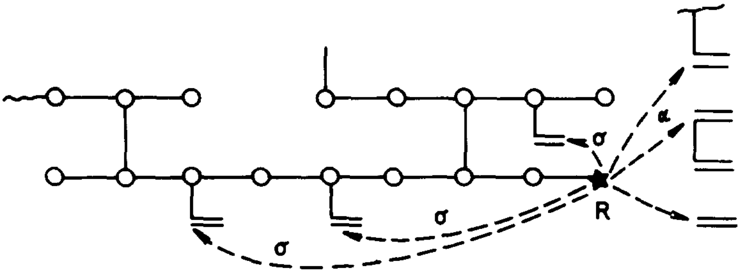

Fig.1

Experimental Evidence

The chain crosslinking (co)polymerization is characterized by the following main experimental features:

(1) Gelation in a ring-free system should occur if one crosslink issues from one weight average primary chain (one repeat unit in the chain is crosslinked). Experimental critical conversions of monomers are however shifted towards higher values by a factor of the order of magnitude 10^0-10^2. This factor increases with increasing content of the bisunsaturated monomer and increasing degree of polymerization of the primary chains (cf.e.g. HOLT and SIMPSON 1965, SPURR et al. 1959, STOREY 1965, WESSLAU 1967, MALINSKÝ et al. 1971, ITO et al. 1975, OKASHA et al. 1980, GALINA et al. 1980). The smallest shift is observed for very low concentrations of the bisunsaturated monomers and very short primary chains (e.g., diallyl phthalate). As expected, critical conversion increases with dilution.

(2) The content of double reacted divinyl units in low-conversion (co)polymers is relatively high, usually considerably exceeding the value needed for attaining the gel point in a ring-free system. Especially in copolymers with a higher content of bisunsaturated component, unsaturation varies with conversion only very little or not at all. In the same systems, unsaturation (or the fraction of double reacted divinyl units) usually varies only little with dilution (cf. e.g. HAWARD 1954, HOLT and SIMPSON 1956, MINNEMA and STAVERMAN 1968, ASO 1959, WESSLAU 1967, MALINSKÝ et al. 1971, SOPER et al. 1972, BRAUN and BRENDLEIN 1973b, FUNKE et al. 1975, ITO et al. 1975, SHAH et al. 1978, DUŠEK and SPĚVÁČEK 1980, GALINA et al. 1980). On the other hand, OKASHA et al. (1979) found the content of units with pendant vinyl only somewhat lower than that of all the divinyl units in the copolymer.

(3) Copolymerization of methyl methacrylate with pendant double bonds of poly(ethylene dimethacrylate) is slower than with double bonds of ethylene dimethacrylate (ASO 1959).

(4) With increasing length (flexibility) of the bridge in the divinyl component, there is a decrease in unsaturation and an increase in the fraction of double reacted divinyl units, both intra- and intermolecularly (SHAH et al. 1978).

(5) Molecular masses of low-conversion (co)polymers are much lower than values corresponding to a ring-free reaction, being in the extreme case close to molecular masses of primary chains (GALINA et al. 1980). The study of copolymers with degradable crosslinks has revealed that the fraction of intermolecular crosslinks is low (MINNEMA and STAVERMAN 1958, BRAUN and BRENDLEIN 1973, MRKVIČKOVÁ and KRATOCHVÍL 1980), much more crosslinks are of the ring-forming type.

(6) The intrinsic viscosity of low-conversion (co)polymers is very low with the exception of the range close to the gel point and rather decreases with the content of the divinyl component of the copolymer

(cf.e.g. ZIMM et al. 1958, SOPER et al. 1972, GALINA et al. 1980). It is much lower than the value calculated for randomly distributed branches. It is also close to the intrinsic viscosity of microgels with the same molecular mass obtained by emulsion copolymerization (HOFFMANN 1974).

(7) In low-conversion soluble copolymers of styrene and ethylene dimethacrylate only one part of the copolymer is reflected in high-resolution ^{1}H-NMR spectra; the "invisible" fraction increases with increasing content of the divinyl component (SPĚVÁČEK and DUŠEK 1980).

(8) Sometimes at a high content of the divinyl component the sample becomes temporarily turbid beyond the gel point, which indicates a certain inhomogeneity (HORIE et al. 1975).

Discussion

The experimental data given above provide sufficient experimental evidence on the importance of cyclization, but also indicate the possibility of a considerably reduced reactivity of the pendant vinyl.

The shift of the gel point may be alternatively explained by the (extremely) low reactivity of pendant vinyls or by strong cyclization, but the comparatively high content of double reacted bisunsaturated units already at the very beginning of the reaction, the low fraction of intermolecular crosslinks with respect to their total number, the extremely low intrinsic viscosities of low-conversion polymers and their compactness unambiguously suggest cyclization. On the other hand, there exists experimental evidence that the apparent reactivity of the pendant vinyl may be very low: the lower copolymerization rate of the pendant vinyl, the weak dependence or independence of the unsaturation of (co)polymers on conversion up to high conversions or an increase in the fraction of units with pendant double bonds with increasing concentration of the bisunsaturated monomer. A question thus arises why the extent of cyclization decreases with the increasing content of units of the bisunsaturated monomer in the polymer, while according to Fig.1 it should increase (there are several possibilities how to close a ring).

This seeming paradox can be resolved taking into account that it is just cyclization, which forms internally crosslinked and rigid structures with pendant double bonds "buried" inside. The ability of the internal double bonds to react, even with small mobile molecules of monomers, is much reduced or completely suppressed. MINNEMA and STAVERMAN (1958) called this phenomenon shielding. The rigid structure may be loosened by e.g. extending the separation of double bonds in the crosslinking agent, which leads to a rise in the apparent reactivity of the pendant vinyl. The compact character of structures with a higher content of the crosslinking agent, which have the character of microgel particles, is demonstrated experimentally by intrinsic viscosity measurements or NMR spectra.

The mechanism of network formation via formation of microgel-like particles due to cyclization and their interlinking has also been put forward in a recent monograph (IRZHAK et al. 1979).

Thus, the apparent decrease in reactivity is given by physical factors due to cyclization, and changes in chemical reactivity given by the (possibly) different chemical structure of the bisunsaturated monomer and its copolymerization behaviour are of secondary importance. The effect of the various and variable (substitution effect) reactivity of double bonds in the bisunsaturated monomer in the copolymerization has been theoretically treated for ring-free systems (cf. e.g. GIBBS 1964, WESSLAU 1967, DUŠEK 1969, BRAUN and BREDLEIN 1973a), but - as has been shown above - the use of ring-free approximation is rather questionable. Theoretical approaches involving ring formation also exist, but they do not take into account the effect of rings already formed on the cyclization probability, and may therefore be utilized only in cases with a low number of rings per primary chain, and hence for a low content of the bisunsaturated monomer (DUŠEK and SPĚVÁČEK 1980).

Thus, network formation in the chain (co)polymerization of the bisunsaturated monomer proceeds approximately so as shown in Fig.2: primarily, compact internally crosslinked particles possessing microgel character are formed, which are linked through their peripheric double bonds to yield a gel. Such a course is typical of medium and high contents of the bisunsaturated monomer. Dilution of the system supports intraparticle contacts, and this is the main reason why the gel point is shifted towards higher conversions. Cyclization measured by the concentration of intramolecular crosslinks increases only little with dilution, because dilution has only a small effect on the internal structure of the particles. At a low content of the bisunsaturated component and low degrees of polymerization of primary chains, the course approaches the classical crosslinking process, where linking of branched coils is assumed. However, cyclization can never be eliminated, unless the forming chains are extremely rigid.

At medium and high contents of the bisunsaturated monomer, network formation rather resembles flocculation of suspended particles, and a rather heterogeneous gel structure may be expected. Paradoxically, copolymers crosslinked to high conversions appear e.g. mechanically quite homogeneous. This paradox may be solved by assuming that interparticle spaces are

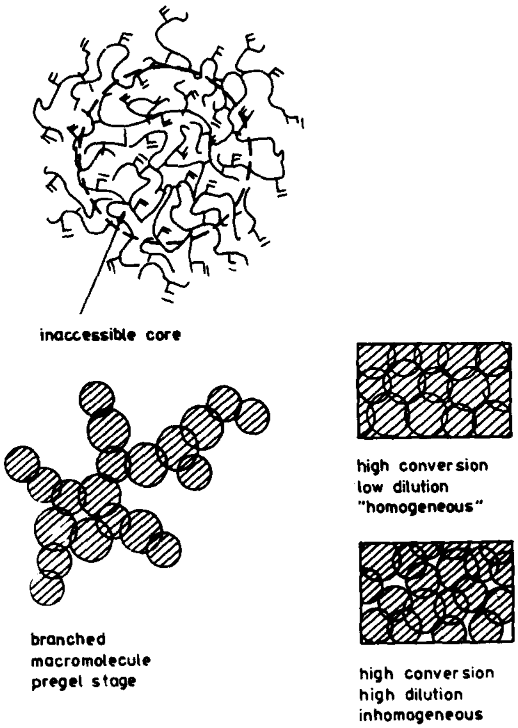

Fig.2

gradually filled in with the forming (co)polymer during polymerization beyond the gel point (occuring usually at a conversion below 10%), and differences in segmental densities become more or less smoothed out. If an inert solvent is added to the system, which is usual in the preparation of macroporous structures, heterogeneity is preserved.

It seems evident, therefore, that networks obtained by the chain crosslinking (co)polymerization may be suitably used as model networks perhaps only in the extreme case of the lowest concentrations of the bisunsaturated monomer. Investigation of the inhomogeneity of such networks close beyond the gel point and of the effect of inhomogeneity on their properties calls for a more detailed study.

Note added: Before mailing this paper the authors have come across the recent fundamental study of the crosslinking copolymerization of methyl methacrylate by R.S. WHITNEY and W.BURCHARD (Makromol.Chem. 181,869 (1980)). Their results confirm the decisive role of cyclization and nonhomogeneous course of network formation.

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