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Network formation in the free-radical copolymerization of a bismaleimide and styrene

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Network formation during copolymerization of styrene with a model bismaleimide, *p*-maleimidobenzoic anhydride, or with mixtures of *p*-maleimidobenzoic anhydride and methyl *p*-maleimidobenzoate was studied. The concentrations of pendent double bonds in copolymers, calculated from the consumption of monomers and copolymer composition, follow the general trend typical for vinyl–divinyl copolymerizations. A substantial fraction of pendent maleimide bonds remains in the system at the end of polymerization. The gel point conversions are much higher than for ring-free copolymerizations due to cyclization and steric hindrance of pendent double bonds. The gel point conversions increase with increasing content of the monomaleimide in the copolymerization mixture reaching 100% at 4 mol% of bismaleimide (12 wt% solution). The gel point conversions also increase with increasing dilution reaching 100% for the bismaleimide polymerization in 3 wt% solution. The steric hindrance effect on pendent double bond reactivity seems to be somewhat higher than for conventional vinyl–divinyl copolymerizations. Copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: bismaleimide; styrene; network formation)

INTRODUCTION

The copolymerization of a model bismaleimide (*p*-maleimidobenzoic anhydride) with styrene was studied experimentally in a recent paper[1]. This study was complemented by studies of copolymerization of a monounsaturated analogue of bismaleimide, methyl *p*-maleimidobenzoate, which revealed that the copolymerization was close to the alternating one. Moreover, this study enabled the estimation of molecular weights of primary chains formed in bismaleimide copolymerization and their variation with the concentration of initiator, solvent, etc.

On the other hand, the *p*-maleimidobenzoic anhydride (*p*-MBAA) units in branched structures and in the gel could be hydrolysed to yield *p*-maleimidobenzoic acid–styrene chains and thus the primary molecular weights and units with pendent double bonds could be determined directly. It was found that the weight-average molecular weights of primary chains in the gel fraction, w_g ($w_g < 1$), are higher than those obtained by linear copolymerization of methyl *p*-maleimidobenzoate (*p*-MMB) with styrene. This finding can be explained by the usual preferential crosslinking of components of higher functionality (the functionality is proportional to the degree of polymerization of primary chains) as well as by the retardation of bimolecular termination in the gel (gel or Trommsdorff effect). The high values of the critical conversion at the gel point (the ratio between the experimental and ideal values of the critical conversion amounted to about 10^2) indicated a very non-ideal network formation, typical of free-radical crosslinking copolymerizations[2].

Special features of network build-up and theoretical models

When a bisunsaturated monomer adds to a growing chain, one of its double bonds reacts while the other one remains unreacted (pendent). The pendent double bonds take part in the copolymerization process as a result of which the fraction of units of the bisunsaturated monomer with pendent double bond decreases with increasing conversion, in the ideal case, from unity to zero. The main parameters which govern network build-up are the degree of polymerization of primary chains (weight average, P_w^0), the fraction of units of the bisunsaturated monomer in the polymer chains, and conversion of double bonds and, possibly, the difference in chemical reactivity of double bonds either intrinsic or induced (substitution effect). The expected values of the gel point conversion for ring-free polymerizations are of the order of 10^{-2}–10^{-4} for $P_w^0 = 10^2$–10^4.

However, such values have almost never been found. Cyclization and/or decrease in reactivity of the pendent

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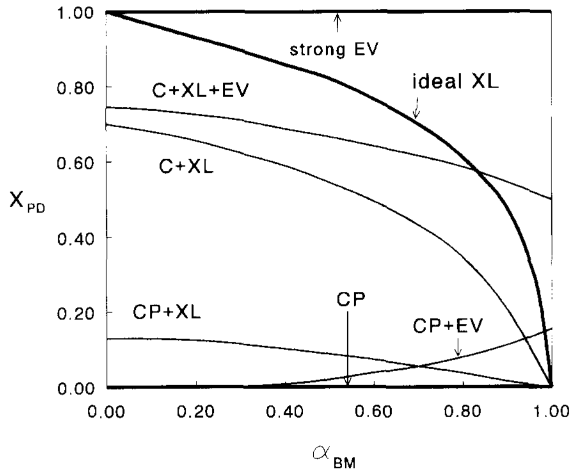

Figure 1 Schematic dependence of the fraction of pendent double bonds on conversion of a bismaleimide. XL, Crosslinking; EV, excluded volume; C, cyclization; CP, cyclopolymerization

double bonds are the main reasons. We will first consider them separately and then their combined action. Typical dependences of the fraction of pendent double bonds, x_{PD}, ([units of bisunsaturated polymer with pendent double bond]/[all units of bisunsaturated monomer in the polymer]) are shown in *Figure 1*. In case of the ideal ring-free copolymerization (see below) the fraction of units with pendent double bonds gradually decreases from 1 to 0.

Cyclization (C) can be short-range and long-range. Very strong short-range cyclization results in cyclopolymerization (CP)[3] and all pendent double bonds immediately react with the free radicals at the chain ends. As a result, the chains are linear, the concentration of pendent double bonds is always zero, and there is no gelation. A long-range cyclization (C) involves closures of rings of variable sizes by attacks of pendent double bonds located at different distances by a free radical in the same molecule and cannot occur without crosslinking (XL). In this situation, a certain number of pendent double bonds exists, and competitive intermolecular crosslinking can occur.

A decrease in the reactivity of pendent double bonds can be caused by chemical or steric reasons (excluded volume effect, EV). If the decrease is very strong, then up to conversion of double bonds equal to half, the fraction of units with pendent double bonds remains unity, and the conversion can increase beyond this limit only by inter- or intramolecular crosslinking. Often, the decrease in the effective reactivity of pendent double bonds is caused by steric hindrances due to cyclization.

Combination of cyclization and decreased reactivity of pendent double bonds (C + XL + EV) is the most typical case in crosslinking polymerizations[2]. Strong cyclization relative to intermolecular crosslinking occurs at the beginning of polymerization just because the probability that the macroradical end meets a pendent double bond on another chain converges to zero in the limit of zero conversion. At the same time, the probability that the free radical meets a pendent double bond in the same molecule is finite. Intramolecularly crosslinked chains are formed first. The reactivity of pendent double bonds in their interior is low because the macroradicals cannot penetrate the interior of these crosslinked coils. Branching and gelation occur under participation of only the peripheral double bonds. As a result, gelation is strongly delayed and after polymerization a great portion of pendent double bonds remain unreacted despite a relatively high concentration of free radicals[4].

From the point of view of theoretical modelling, the free-radical crosslinking copolymerization is the most complex network formation process for several reasons: (1) the reaction mechanism is complicated and involves several reaction steps; (2) the network build-up is complicated by strong long-range spatial correlations such as cyclization and excluded volume effects; (3) at a certain stage many reaction steps become diffusion controlled.

The problem of the complicated reaction mechanism itself can be successfully solved by the kinetic theory or combinations of kinetic and statistical theories[5-10]. Inclusion of cyclization is a problem.

Of the existing groups of network formation theories[5] – statistical, kinetic (coagulation), and simulation in space – the modification of the statistical theories of structure build-up by combining monomeric units (and the corresponding modifications to deal with cyclization, e.g. the spanning-tree approximation) are not applicable because these theories cannot take into account correctly the complicated reaction mechanisms.

More useful are the other two groups. Among them, the so-called combined method based on kinetic generation of primary chains with distributions of intermolecularly and intramolecularly crosslinked units (halves of bisunsaturated units) and their combination can be a promising approximation for low degrees of cyclization.

Formally, one can add to the essentially bimolecular intermolecular reaction steps a cyclization term, the intensity of which is governed by a cyclization constant (prefactor). However, this prefactor is not a constant at all and varies with conversion. Moreover, the cyclization intensity depends on the number and accessibility of nearer and farther unsaturated groups from the selected free radical and thus the molecule size and structure. Cyclization involves reaction steps of unequal intensity like propagation, transfer and termination reactions which under certain conditions can be diffusion controlled. Moreover, beyond the gel point the term 'cyclization' must be defined by the purpose (e.g. elastically inactive cycles[11,12]) because beyond the gel point cyclization occurs anyway (build-up of cycle rank). This is just a reminder of how complicated free-radical crosslinking copolymerization can be and that we are still far away from a realistic quantitative model.

Lattice percolation of initiated polymerizations without taking into account the details of the process and conformational control of the cyclization reactions has brought qualitatively correct features pointing to the importance of cyclization[13]. Because of the reasons given in the preceding paragraph, quantitative predictions are still difficult.

In view of the unsatisfactory state of the theories modelling the free-radical crosslinking copolymerization, we have not attempted to analyse quantitatively the experimental data on copolymerization of bismaleimide monomers in terms of the elaborate but still unsatisfactory models. The goal was to characterize the general features of this process in terms of deviations from the ideal ring-free copolymerization. In this paper, the network formation in the system bismaleimide–styrene is studied in more detail and is complemented by the studies of ternary systems bismaleimide–monomaleimide–styrene. The main parameters to be compared are the concentration of pendent double bonds as a function of conversion and the gel point conversion in dependence on the initial composition and presence of a diluent during polymerization. Limited solubility of the bismaleimide in styrene was a drawback of the system, so that additional solvents (dimethylacetamide or dimethylformamide) had to be used.

EXPERIMENTAL

Materials

Styrene (ST) was dried using molecular sieves and redistilled at reduced pressure. *p*-Maleimidomethyl benzoate (*p*-MMB) and *p*-maleimidobenzoic anhydride (*p*-MBAA) were prepared and characterized as described in ref. 1. Other solvents and chemicals were obtained from Fluka and Aldrich Co. and were used as received.

Polymerizations

Equivalent mixtures of styrene and monomers with maleimide groups in dimethylacetamide were copolymerized in the presence of the free-radical initiator azobis(isobutyronitrile) (AIBN) (0.15–4.5 wt%) at temperatures of 60–70°C. The polymerizations proceeded in sealed glass ampoules in a nitrogen atmosphere. The polymerizations were stopped by diluting the system with DMF or tetrahydrofuran (THF) and cooling it down to −60°C. Crosslinked samples were swelled in DMF. To prevent further polymerization, the solvents contained 0.2% of 2,6-di-tert-butylmethyl-4-phenol (TBMP) as free-radical scavenger.

Analysis of the system

The gelation was detected visually as the time when the loss of fluidity of the system was observed. The increase of viscosity was quite steep with a good reproducibility. The reaction was stopped as described above and the system was analysed. The gel point was also determined by extrapolating the weight fraction of the gel to zero. Good agreement between results obtained by both methods was found.

The pre-gelation samples were analysed by precipitation of the polymer with methanol, the precipitate was filtered off and the concentration of monomers was determined by high-pressure liquid chromatography (h.p.l.c.). Post-gelation samples were extracted several times at room temperature by DMF and the monomers were determined in the combined extracts. The sample was then reswelled in THF and dried *in vacuo* to constant weight. The fraction of the gel, w_g, was determined as the ratio of the mass of dry extracted gel to the initial mass of the monomers.

Spectra Physics SP8100 liquid chromatograph was used for h.p.l.c. and size exclusion chromatography (s.e.c.) measurements. For h.p.l.c, a glass column packed with the reverse-phase Sepharon SIX C18 (particle size 5 μm; Laboratory Instruments) was used. Gradient elution started with 70% water and ended with 100% methanol. The eluted material was detected at wavelength 260 nm. For s.e.c., a set of three columns packed with macroporous silicagel suitable for the molecular mass range 2×10^3–2.7×10^6 was used. DMF was used as eluent with detection at 270 nm. The monomers and stabilizer were not considered to contribute to the polymer distribution.

The composition of the copolymers was determined from elemental analysis and calculated from the consumption of monomers determined by chromatography. It was also checked by ^{13}C nuclear magnetic resonance (n.m.r.) spectra using a Brucker AC-300 instrument; 2–5% of maleimide dyads were found.

Calculation of fraction of pendent double bonds

Pendent double bonds can be obtained directly by hydrolysis of the MBAA–ST copolymer and determination of the monomeric *p*-maleimidobenzoic acid (MBA) by h.p.l.c. However, the separation of the MBA–ST copolymer from the monomeric MBA by precipitation was not easily reproducible which adversely affected the determination of the content of pendent double bonds.

Alternatively, the fraction of pendent double bonds in the copolymer, x_{PD}, can be calculated from the consumption of monomers measured by h.p.l.c. The calculation is based on material balance by which, in the case of an alternating copolymer, in order to connect the reacted MBAA units with pendent double bonds an equal number of styrene molecules is necessary: $c_{ST0} - c_{ST} = c_{BM0} - c_{BM}$, where c_{ST} and c_{BM} are, respectively, the actual concentrations of styrene and bismaleimide and c_{ST0} and c_{BM0} are the respective initial values. If more styrene reacts, it reacts with pendent double bounds. Therefore, the difference

$$(c_{ST0} - c_{ST}) - (c_{BM0} - c_{BM}) = c_{DR} \tag{1}$$

is equal to the concentration of doubly reacted bismaleimide, c_{DR}. The fraction of pendent double bonds, x_{PD}, is equal to the difference between the concentration of both singly and doubly reacted bismaleimide units given by $c_{BM0} - c_{BM}$ and x_{DR} per bismaleimide unit in the polymer

$$\begin{aligned} x_{PD} &= (c_{BM0} - c_{BM} - c_{DR})/(c_{BM0} - c_{BM}) \\ &= 2 - (c_{ST0} - c_{ST})(c_{BM0} - c_{BM}) \end{aligned} \tag{2}$$

If the copolymerization is not alternating, less (excess of maleimide (MI) units in the copolymer) or more (excess of styrene) styrene is necessary than the amount given by equation (1)

$$\begin{aligned} c_{ST0} - c_{ST} &= c_{BM0} - c_{BM} - [(x_{MI} - x_{ST})/x_{MI}] \\ &\quad \times (c_{BM0} - c_{BM}) \\ &= (x_{ST}/x_{MI})(c_{BM0} - c_{BM}) \end{aligned} \tag{3}$$

where x_{ST} and x_{MI} are molar fractions of styrene and maleimide units, respectively, in a linear (primary) chain, so that

$$x_{PD} = 1 + (x_{ST}/x_{MI}) - (c_{ST0} - c_{ST})/(c_{BM0} - c_{BM}) \tag{4}$$

For $x_{ST}/x_{MI} = 1$, equation (2) results.

When monomaleimide with double bonds of the same reactivity as in bismaleimide is present, then the balance reads

$$c_{ST0} - c_{ST} = (x_{ST}/x_{MI})[(c_{BM0} - c_{BM}) + (c_{MM0} - c_{MM})] \tag{5}$$

and

$$x_{PD} = 1 + (x_{ST}/x_{MI}) + (x_{ST}/x_{MI})(c_{MM0} - c_{MM})/(c_{BM0} - c_{BM}) - (c_{ST0} - c_{ST})/(c_{BM0} - c_{BM}) \qquad (6)$$

This relation can be transformed into a dependence on conversions of styrene and bismaleimide, α_{ST} and α_{BM}, respectively

$$x_{PD} = 1 + x_{ST}/x_{MI} + (x_{ST}/x_{MI})(c_{MM0}/c_{BM0}) \times [1 - (1 - \alpha_{BM})^{1/2}]/\alpha_{BM} - (c_{ST0}/c_{BM0})(\alpha_{ST0}/\alpha_{BM0}) \qquad (7)$$

because $1 - \alpha_{BM} = (1 - \alpha_{MM})^2$.

RESULTS AND DISCUSSION

The objective of this work is to compare, in terms of network formation, the free-radical copolymerization of bismaleimides and the free-radical polymerization and copolymerization of conventional divinyl monomers like ethylene dimethacrylate or divinylbenzene. The typical properties of the latter systems are a lower concentration of pendent double bonds in the initial copolymerization products (at 1–2% monomer conversion) than would correspond to the ideal copolymerization (≈ 100%), a large fraction of unreacted double bonds at high conversions of the monomer, and large critical conversions[2].

The bismaleimide used in this study appeared to be poorly soluble in styrene, so that crosslinking in solution had to be used. On the other hand, the presence of a monounsaturated monomer with equal reactivity of maleimide groups enabled us to broaden the range of crosslinking densities and gel point conversions.

Before analysing the network build-up, some preliminary studies were carried out concerning the copolymer composition, molecular weights of the primary chains and the reactivity of maleimide double bonds.

Preliminary studies

The maleimide–styrene copolymers were found to be nearly alternating[1,14]. From the monomer consumption of styrene (ST) and methyl *p*-maleimido benzoate (*p*-MMB) of ref. 1, it follows that the average value of the ratio of consumed *p*-MMB or styrene, which is equal to the composition of the copolymer $F_M = (c_{MM0} - c_{MM})/(c_{ST0} - c_{ST})$, is about 1.05–1.06. In our study using similar techniques, a value of 1.06–1.08 was found (*Figure 2*). There seems to be slight excess of the maleimide units. However, this is not a key factor with respect to the network build-up. The composition of the primary chains is important for calculation of the fraction of pendent double bonds, but only in the region of small conversions where, as we shall see later, the sensitivity of the results to the experimental error in determination of unreacted monomers is quite large.

The other issue concerns the question of whether the double bonds of *p*-MBAA and *p*-MMB are equally reactive or not. This question can be answered by measuring the relative rate of consumption of these two monomers, but not by the relative rate of consumption of the double bonds of these monomers. The fate of the pendent double bonds of incorporated *p*-MBAA is probably influenced by other factors like cyclization and diffusion. The initial steady-state consumption rates of these monomers in the case of equal reactivity are described by the equations

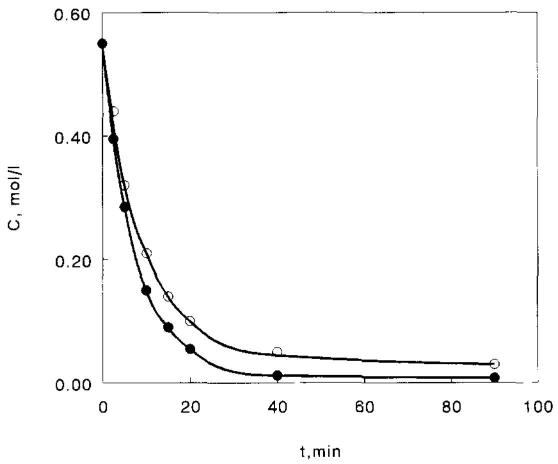

Figure 2 Kinetics of copolymerization of the monomaleimide *p*-MMB with styrene. $T = 60°C$, $C_M = 23$ wt%, $C_{AIBN} = 3$ wt%. ○, Styrene; ●, *p*-MMB

$$d[p\text{-MBAA}]/dt = 2k[R*][p\text{-MBAA}] \qquad (8)$$

$$d[p\text{-MMB}]/dt = k[R*][p\text{-MMB}] \qquad (9)$$

where $k[R*]$ represents the sum of the products of the propagation rate constant and concentration of the respective free radicals. The factor of 2 reflects the fact that *p*-MBAA has two maleimide groups. *Figure 3* shows a satisfactory linear plot of $2\log([p\text{-MMB}]_0/[p\text{-MMB}])$ vs. $\log([p\text{-MBAA}]_0/[p\text{-MBAA}])$ with a slope equal to unity which confirms the equal reactivity of maleimide groups in both monomers.

Pendent double bonds

Unfortunately, it was not possible to isolate the polymer before the gel point by precipitation and to measure the unsaturation of the polymer. The fraction of

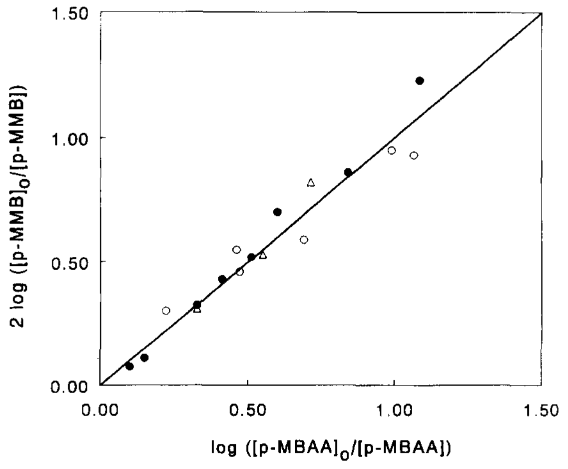

Figure 3 Kinetic dependence of a consumption of *p*-MMB and MBAA in ternary systems ST/*p*-MMB/MBAA. ○, $p'_A = 0.5$; ●, $p'_A = 0.25$; △, $p'_A = 0.09$.

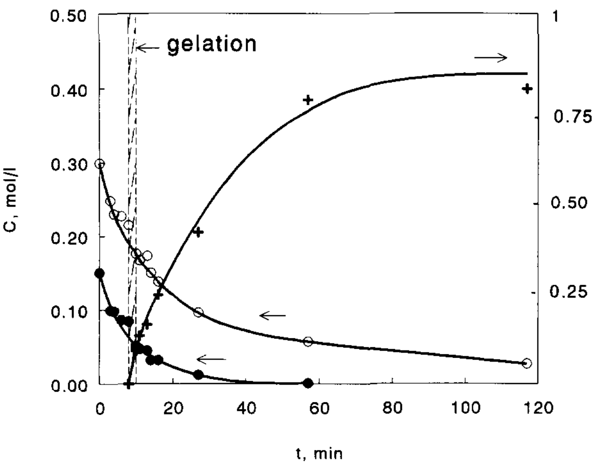

Figure 4 Copolymerization of the system ST/p-MMB/MBAA. $p'_A = 1$, $C_M = 10$ wt%, $C_{AIBN} = 3$ wt%, $T = 70°C$. ○, Styrene; ●, MBAA, $+w_g$

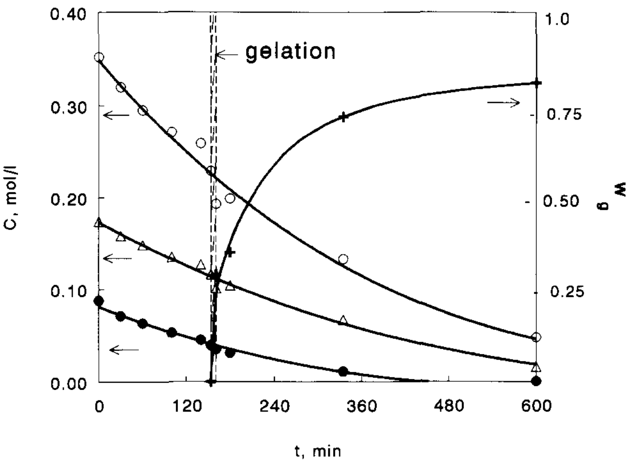

Figure 6 Copolymerization of the system S/p-MMB/MBAA. $p'_A = 0.5$, $C_M = 12$ wt%, $C_{AIBN} = 3\%$, $T = 60°C$. ○, Styrene; ●, MBAA; △, p-MMB, $+w_g$

units with pendent double bonds x_{PD} was therefore calculated from the consumption of monomers as explained in the Experimental section. The monomer concentrations plotted against time for several runs differing in the fraction of monomaleimide or solvent concentration are depicted in *Figures 4–7*.

The values of x_{PD} calculated using this method depend on the composition of primary chains. If they are richer in the bisunsaturated monomer p-MBAA, the value of x_{PD} is lower (cf. equations (2) and (4)). From data of ref. 1 the molar ratio of p-MMB to ST units in the copolymer is about 1.05–1.06 and a slightly higher ratio was obtained in these studies. Therefore, for the calculation the value of 1.06 was taken. Taking 1.06 instead of 1.00 (strictly alternating case), alters x_{PD} by about 0.10, so that the difference is not great. Furthermore, it should not be forgotten that at the beginning of the copolymerization the values of x_{PD} are obtained from differences between relatively large values of monomer concentrations (equation (2)), which introduces large errors. The precision of chromatographic determination of the monomers is ±2% and this, at the p-MBAA conversion of 10%, can produce a fluctuation ±0.6 in the value of x_{PD}. This means that using this method, any physical interpretation of the values of x_{PD}. This means that using this method, any physical interpretation of the values of x_{PD} in this region is meaningless. Also, with increasing concentration of the monounsaturated p-MMB the precision of the x_{PD} values decreases.

With these reservations in mind, one should consider the results summarized in *Figure 8*. Discarding the data at low conversions, one can say that data at intermediate conversions are not far from the values for ideal copolymerization. At high conversion, however, the unreacted double bonds always exist in the system while in ideal copolymerization all of them eventually react. In fact, the middle and high conversion parts of the curves do not differ from the typical dependences obtained for non-ideal divinyl polymerizations and copolymerization[2] where the network formation is a result of an interplay of two factors: cyclization and a (sterically) diffusion-controlled decrease in the reactivity of pendent double bonds leading to network formation via the microgelation mechanism. For determination of the intensity of cyclization, the low conversion values of x_{PD} would be necessary but, unfortunately, they cannot be obtained with sufficient precision. For characterization

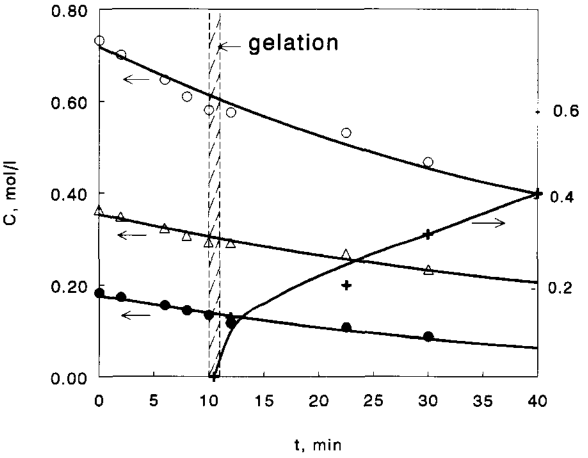

Figure 5 Copolymerization of the system ST/p-MMB/MBAA. $p'_A = 0.5$, $C_M = 25$ wt%, $C_{AIBN} = 3\%$, $T = 60°C$. ○, Styrene; ●, MBAA; △, p-MMB, $+w_g$

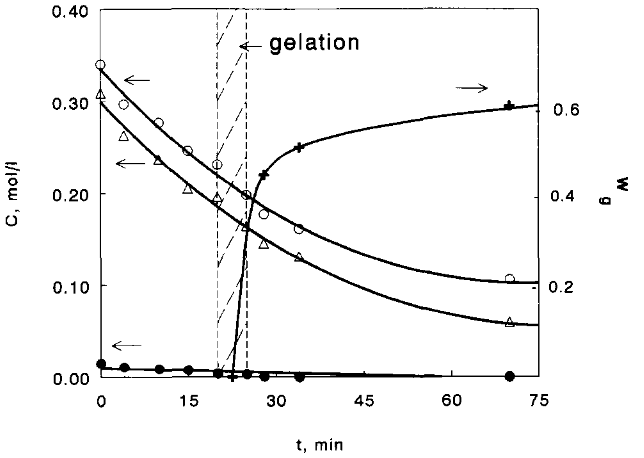

Figure 7 Copolymerization of the system ST/p-MMB/MBAA. $p'_A = 0.085$, $C_M = 12$ wt%, $C_{AIBN} = 3$ wt%, $T = 60°C$. ○, Styrene; ●, MBAA; △, p-MMB, $+w_g$

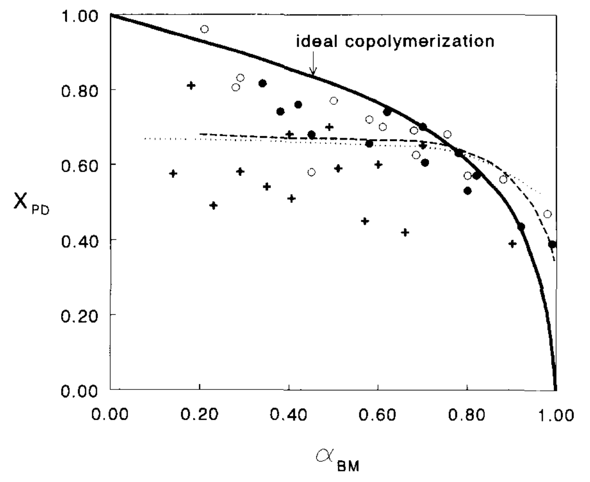

Figure 8 Dependence of fraction of units with pendent double bonds from monomer consumption (equations (6) and (7)). —, Theoretical curve for ideal ring-free copolymerization; - - -, poly(1,6-hexanedioldiacrylates[4]; ···, styrene–15% *m*-divinylbenzene copolymers[24]; ○, data from ref. 1, recalculated; ●, data from this work $p'_A = 1$; +, this work $p'_A = 0.5$

of the deviations from ideality, the gel point conversion is thus more important.

Nevertheless, one can compare the present results with the best fit of data obtained earlier for poly(1,6-hexanediol diacrylate)s and styrene–divinylbenzene copolymers (*Figure 8*). It appears that the bismaleimide systems may rank among the systems with somewhat higher concentration of pendent double bonds. This may mean that cyclization is somewhat weaker, or, more probably, that the excluded volume effect induced by cyclization is stronger and sets in at earlier stages of polymerization.

Gel point conversions

The critical conversions, α_c, of monomers at the gel point are much higher than those calculated theoretically. The respective relations have been derived for a ring-free system in Appendix A (see equations (A7), (A10), (A13), (A16), (A17) or (A18)). The values of the critical conversion are displayed in *Figure 9*. Changing the fraction of the bisunsaturated monomer *p*-MBAA, p'_A, from 1 down to 0.04, the critical conversions of *p*-MBAA increase from 0.6 to almost 1. The theoretical (ring-free) conversion of double bonds, taking for the weight-average degree of polymerization of primary chains, P_w^0, the value approximately equal to 800 (ref. 1), varies from 0.005 to 0.12. This means that most of the bonds have been lost in intramolecular reactions and only about 0.8% (*p*-MBAA/ST copolymer) to 12% (*p*-MBAA/*p*-MMB/ST copolymer, $p'_A = 0.04$) of the *p*-MBAA crosslinks have been active in intermolecular branching.

The observed large shift in critical conversions is always due to the combined effect of cyclization and inaccessibility of pendent double bonds inside the microgels (steric excluded volume). The latter effect is important from the beginning of polymerization. The increase in molecular weights and gelation can be considered as corresponding to intermolecular reations of groups located in the surface shell of the microgel-like particles. Within this concept, one can consider the thickness of this shell (for the case of equation (A16)) to be given by the relation

$$(\alpha_{BM})_c = 1 - \{1 - 1/[p'_A(m(P_w^0)^{2/3}(h/h_0) - 1)]\}^2 \quad (10)$$

in which P_w^0 has been replaced by the effective volume of the surface layer of the spherical particles $(P_w^0)^{2/3}(h/h_0)$. Here, h/h_0 is the relative thickness of this layer. For the two limiting cases given above, h/h_0 amounts to 0.04 (quite compact) and 0.24 for $p'_A = 0.09$ which means that in this case the obstruction is not so severe.

It must not be forgotten that all polymerizations took place in a solvent, the presence of which always promotes cyclization. With increasing concentration of solvent, the gel point conversion was further shifted to higher values and, for a given composition, there existed a limiting concentration of solvent at which the gel was not formed at all (*Figure 10*). This concentration was 3 wt% for $p'_A = 1$ and 5.5 wt% for $p'_A = 0.05$. This concentration dependence can also be used for the estimation of cyclization of bismaleimides of similar structure in bulk.

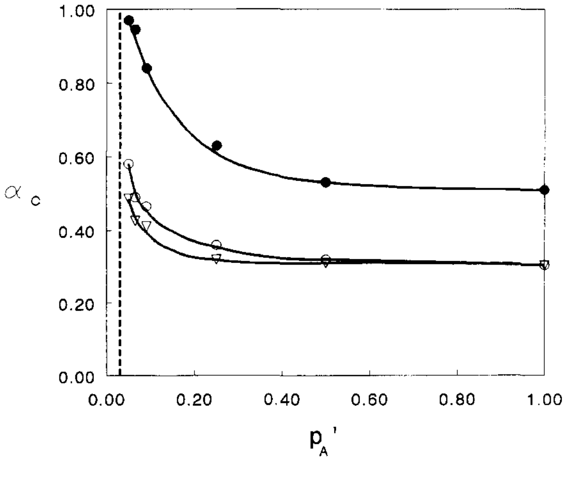

Figure 9 Critical conversion of the monomers at copolymerization of the system ST/*p*-MMB/MBAA as a function of the fraction of the crosslinker p'_A. $C_M = 12$ wt%, $C_{AIBN} = 3$ wt%, $T = 60$°C. ○, Styrene; ●, MBAA; △, *p*-MMB

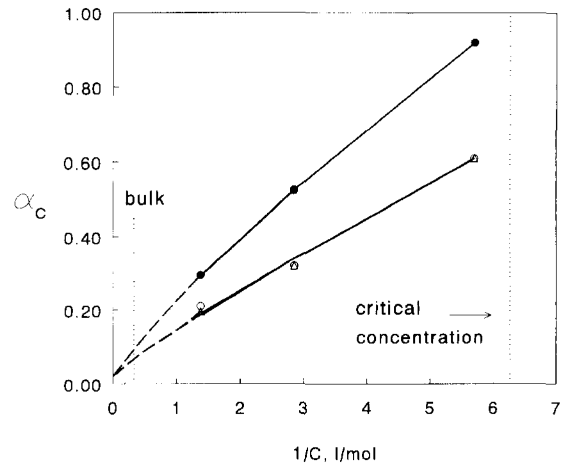

Figure 10 Critical conversion of the monomers in the system ST/*p*-MMB/MBAA as a function of dilution. $p'_A = 0.5$, $C_{AIBN} = 3$ wt%, $T = 60$°C. ○, Styrene; ●, MBAA; △, *p*-MMB

The extrapolated value of $(\alpha_S)_c$ for bulk polymerization of *p*-MBAA of about 0.07 is still an order of magnitude higher than that corresponding to a ring-free case.

A direct comparison with gel point conversions of other divinyl monomers like diacrylates[4] or dimethacrylates, divinylbenzene and styrene–divinylbenzene copolymers[2] is difficult due to the fact that solution polymerization often results in phase separation. For bismaleimides, the presence of highly solvating solvent used in this study prevents the system from phase separation and can additionally retard macroscopic gelation.

The development of the gel fraction, w_g (*Figures 4–7*) is also interesting. The initial increase is steep and corresponds to the transformation of the existing polymer molecules from the sol into the gel. However, the further increase in w_g follows, more or less, the consumption of the monomers. This means that during polymerization the newly formed polymer chains become immediately attached to the gel through one or more pendent double bonds in the gel. Such behaviour differs from stepwise network build-up where the gel fraction in the later stages changes with conversion only very little since the molecular weight of the sol steeply decreases with conversion.

Molecular weights of primary chains in gel

The molecular weights of *p*-MMB copolymers (M^0) studied in ref. 1, corresponding to primary chains, are of the order of 4×10^4 for M_w^0 and 2×10^4 for M_n^0. After hydrolysis of the *p*-MBAA network, a considerably higher M_w^0 (up to 10^5) of primary chains in the whole system was found. For the whole system near the gel point M_w^0 was about 8×10^4 and M_w^0 of the gel fraction was about 11×10^4. The increase of M in the whole system can be explained by the Trommsdorff (gel) effect. However, M_n^0 did not change much, which means that the polydispersity increased as a result of the Trommsdorff effect. Again, for the ideal crosslinking between primary chains, one can calculate theoretically how the distribution of primary chains in the gel should change. The results are given in Appendix B. The weight-average molecular weight of primary chains contained in the gel should be equal to the *z*-average molecular weight in the whole system so that

$$(M_w^0)_{gel}/(M^0_{gel+sol}) = (M_z^0)_{gel+sol}/(M_w^0)_{gel+sol} \qquad (11)$$

For the most probable distribution of primary chains and $M \gg 1$

$$(M_z^0)/(M_w^0) = 3/2 \qquad (12)$$

For this experimental system, this ratio is expected to be somewhat higher due to the gel effect on distribution broadening. One can perhaps expect a value close to 2 instead of 1.5. However, the experimental value is about 1.3–1.4. To explain this difference, one should take into account that gelations in the free-radical systems are controlled rather by a microgelation mechanism where the selection of primary chains to join the gel occurs according to their actual functionality which is proportional not to P_w^0 but close to $(P_w^0)^{2/3}$ (cf. discussion in ref. 5).

CONCLUSIONS

From the relative decrease of the concentrations of the monomers during copolymerizations of bismaleimide and monomaleimide with styrene and from determination of gel point conversions it follows that the network formation does not substantially differ in general features from that in free-radical copolymerizations of polyunsaturated monomers. The change in the fraction of pendent double bonds with conversion calculated from relative consumptions of the monomers was not very conclusive; however, it has revealed that a substantial fraction of pendent maleimide bonds remains in the system at the end of polymerization. This is a typical feature of this type of polymerization. The gel point conversions are much higher than would correspond to a ring-free case, which is a consequence of steric hindering of the pendent double bonds in reaction in the later stages of copolymerization and confirms the important role of cyclization in the early stage of copolymerization. With increasing amount of monomaleimide, the network is looser and the network formation is closer to the ideal one, but still far from it.

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APPENDIX A

Gelation in ideal copolymerization

Generally, the composition of the primary chains depends on the reactivity ratio of the double bonds of monomers which determines the composition of instantaneously formed chains and the possible conversion drift. In ideal copolymerization, the composition of the primary chains is constant and equal to the composition of the monomers in the feed and there is no compositional drift.

Close to this case is the binary, nearly alternating, copolymerization of double bonds A of the bisunsaturated monomer AA (bismaleimide) with a monovinyl monomer S (e.g. styrene), or a ternary system of double bonds A of a bisunsaturated monomer and double bonds B of a monounsaturated monomer of the same reactivity as A participating in copolymerization with S. It is the common practice in theoretical network formation treatment[15–17] to generate the resulting structures in three steps. In step 1, the units of the bisunsaturated monomer with groups of independent reactivity are split into two units with double bonds A; in Step 2, primary chains generated by copolymerization of A with S or A and B with S; and in Step 3, the connections between the double bonds A are randomly reformed as in vulcanization of primary chains[5].

The composition of the system in terms of unreacted double bonds and primary chains can be expressed through a generating function

$$\begin{aligned} F_0(z, Z) = [&(1-\alpha_A)p_A Z_A z + (1-\alpha_B)p_B Z_B \\ &+ (1-\alpha_S)p_S Z_S \\ &+ (\alpha/P_n^0)\sum_{i,j,k} n_{ijk} z^i Z_A^i Z_B^j Z_S^k]/(1-\alpha+\alpha/P_n^0) \end{aligned} \tag{A1}$$

where p_A, p_B and p_S are, respectively, molar fractions of unreacted double bonds A, B, and S; P_n^0 is the number-average degree of polymerization of primary chains, n_{ijk} is the number fraction of chains composed of i, j and k units A, B and S, respectively; $\alpha = \alpha p_A + \alpha p_B + \alpha p_S$; z is the variable of the generating function counting the connections between A units in AA, $X = (Z_A, Z_B, Z_S)$ are variables identifying units A, B and S which are useful if one wants to ascribe certain characteristics, like their molecular weights, to these units. The number of molecules in the system is not constant and it changes (decreases) with increasing conversion which is taken into account by the term α/P_n^0.

For the above-mentioned condition of equal reactivity of A and B double bonds, $\alpha_A = \alpha_B = \alpha_M$ (M = maleimide) and

$$\sum n_{ijk} z^i Z_A^i Z_B^j Z_S^k = \sum n_{p\text{-}k,k}(p'_A Z_A z + p_B Z_B)^{p-k} Z_S^k \tag{A2}$$

where $p = i + j + k$, and $p'_A = p_A/(p_A + p_B)$ and $p'_B = 1 - p'_A$.

For alternating copolymers, it also holds, either for an M : S equivalent mixture or for low conversions (no compositional drift), that $\alpha_M = \alpha_S = \alpha$ and $k = p/2$, so that

$$\sum n_{ijk} z^i Z_A^i Z_B^j Z_S^k = \sum n_p (p'_A Z_A z + p'_B Z_B)^{p/2} Z_S^{p/2} \tag{A3}$$

For not strictly alternating but constant composition of primary chains, for instance at low conversions

$$(\alpha_A p_A + \alpha_B p_B)/(\alpha_A p_A + \alpha_B p_B + \alpha_S p_S) = m$$

and it holds that

$$\sum n_{ijk} z^i Z_A^i Z_B^j Z_S^k = \sum n_p (p'_A Z_A z + p'_B Z_B)^{mp} Z_S^{(1-m)p} \tag{A4}$$

Since these equations will be used below for prediction of the gel point conversion under ring-free conditions, we do not have to identify the types of the units in the chains and, therefore, $\boldsymbol{Z} = (Z_A, Z_B, Z_S) = (1, 1, 1)$. For the conditions of equation (A3) (alternating case), equation (A1) gives the following relation

$$\begin{aligned} F_0(z) = \{&(1-\alpha)[1 - p'_A/2 + (p'_A/2)z] \\ &+ (\alpha/P_n^0)\sum n_p (p'_A z + p'_B)^{p/2}\}/(1-\alpha+\alpha/P_n^0) \end{aligned} \tag{A5}$$

The generating function for the number of bonds issuing from a unit (halves of AA and primary chains) looking out of a unit already connected through one bond (when looking in the unit under consideration) with another unit, one gets by differentiation and renormalization

$$F(z) = (1-\alpha) + (\alpha/P_n^0)\sum p n_p (p'_A z + p'_B)^{(p/2)-1} \tag{A6}$$

The gel-point condition is given by the equality

$$[\mathrm{d}F(z)/\mathrm{d}z]_{z=1} = 1$$

i.e. on average one bond issues from a unit already connected with its neighbour. This condition gives the critical conversion at the gel point

$$\alpha_c = 1/[(p'_A)(P_w^0/2 - 1)] \tag{A7}$$

If the alternating character of chains is abandoned but the overall composition of primary chains is the same, i.e. $p_A + p_B = p_S = 1/2$, equation (A3) is substituted by

$$\sum n_{ijk} z^i Z_A^i Z_B^j Z_S^k = \sum n_p (p_A z Z_A + p_B Z_B + p_S Z_S)^p \tag{A8}$$

For $\alpha_A = \alpha_B = \alpha_S$, the function $F(z)$ now becomes

$$F(z) = (1-\alpha) + (\alpha/P_n^0)\sum p n_p (p_A z + 1 - p_A)^{p-1} \tag{A9}$$

and the equation for the critical conversion reads

$$\alpha_c = 1/[(p'_A/2)(P_w^0 - 1)] \tag{A10}$$

which is different from equation (A7) (higher critical conversion in the case of alternating composition), but gives the same asymptotic value for high P_w^0

$$\alpha_c \approx 1/[(p'_A/2)P_w^0] \tag{A11}$$

If equation (A4) is valid,

$$\begin{aligned} F(z) = &(1-\alpha_M) \\ &+ (\alpha m p'_A/P_n^0)\sum p n_p (p'_A z + 1 - p'_A)^{mp-1} \end{aligned} \tag{A12}$$

and

$$\alpha_c = 1/[(m/p_M)p'_A(mP_w^0 - 1)] \tag{A13}$$

which is identical with equation (A7) if $m = 1/2$ and $p_M = 1/2$, the alternating case. The equivalent of equation (A11) then reads

$$\alpha_c = 1/[(m^2/p_M)p'_A P^0_w] \tag{A14}$$

or, since $\alpha_M p_M = \alpha_m$

$$(\alpha_M)_c = 1/(mp'_A P^0_w) \tag{A15}$$

In these experiments, it is not the critical conversion of the double bonds that is measured but the critical conversion of monomers. If it is the critical conversion of bismaleimide, α_{BM}, it is related to α (in the case of alternating character) or α_M through the relation

$$\alpha_M = 1 - (1 - \alpha_{BM})^{1/2}$$

and the critical equation (A13) now reads

$$(\alpha_{BM})_c = 1 - \{1 - 1/[p'_A(mP^0_w - 1)]\}^2 \tag{A16}$$

and for $P^0_w \gg 1$

$$(\alpha_{BM})_c = 1 - (1 - 1/mp'_A P^0_w)^2 \approx 2/mp'_A P^0_w \tag{A17}$$

If the critical conversion of styrene is examined, then

$$(\alpha_S)_c = \{p_M(1-m)/[m(1-p_M)(mp'_A P^0_W)]\} \tag{A18}$$

In the case of conversion shifts, equation (A1) is still valid but the distribution n_{ijk} is a function of conversion. It can be calculated, if the reactivity ratios of the monomers are known, for a batchwise or continuous feed process[18,19].

APPENDIX B

Degree of polymerization averages of primary chains in gel

To derive the relation between the degree of polymerization of primary chains contained in gel in a ring-free random crosslinking, we will again employ the theory of branching process[20–23]. The weight fraction distribution of primary chains in the whole system is given by the weight fraction generating function $W_0(z)$

$$W_0(Z) = \sum w_p Z^p \tag{B1}$$

where w_p is the weight fraction of p-mer. A fraction $1 - \beta$ of units is not crosslinked and a fraction β is crosslinked*. The crosslinked units extend a bond that can have a finite or infinite continuation. The chains that have no crosslinked unit with infinite continuation belong to the sol. The rest of the primary chains are bound in the gel. Whether a bond has finite continuation is determined by the extinction probability, v, which is a conditional probability that, given that the bond exists, the continuation through it looking out of the unit is only finite. The extinction probability is given by the equation

$$\begin{aligned} v &= \sum w_p(1 - \beta + \beta v)^{p-1} \\ w_p &= pn_p \Big/ \sum pn_p \end{aligned} \tag{B2}$$

The sol fraction is composed only of chains that have no unit with bond with infinite continuation (all bonds must have finite continuation). The weight fraction of the sol is given by

$$w_s = \sum w_p(1 - \beta + \beta v)^p \tag{B3}$$

The weight-average degree of polymerization of chains in the gel, $(P^0_w)_{gel}$, is given by the contributions to P^0_w by all chains minus those in sol, divided by the fraction of units in the gel

$$(P^0_w)_{gel} = \frac{\sum pw_p - \sum pw_p(1 - \beta + \beta v)^p}{1 - \sum w_p(1 - \beta + \beta v)^p} \tag{B4}$$

Equation (B4) can be solved for the specific distribution of primary chains that gives closed expressions for the generating function (B1). Such expressions always exist if the distribution can be expresed through Laplace transform[23]. We can show, however, that equation (B4) has a solution in the limit of the gel point at which $v = 1$. At this limit, the numerator and denominator are equal to zero, but using the l'Hospital rule one gets

$$\begin{aligned} \lim[(P^0_w)_{gel}]_{v \to 0} &= \lim \frac{\sum p^2 w_p(1 - \beta + \beta v)^{p-1}}{\sum pw_p(1 - \beta + \beta v)^{p-1}} \\ &= \frac{\sum p^2 w_p}{\sum pw_p} = P^0_z \end{aligned} \tag{B5}$$

The distribution of model primary chains seems to be close to the most probable distribution. For this distribution, the number-fraction generating function, $N(Z)$, reads

$$N(Z) = \sum n_p Z^p = \sum (1 - q)q^{p-1} Z^p = \frac{(1 - q)Z}{(1 - qZ)} \tag{B6}$$

where

$$q = 1 - 1/P^0_n$$

The generating functions giving higher averages can be obtained successively

$$\begin{aligned} W(Z) &= \left(\sum pn_p Z^p\right) \Big/ \left(\sum pn_p\right) \\ &= ZN'(Z)/N'(1) = \frac{(1 - q)^2 z}{(1 - qz)^2} \end{aligned} \tag{B7}$$

$$\begin{aligned} Z(Z) &= \left(\sum p^2 n_p Z^p\right) \Big/ \left(\sum p^2 n_p\right) \\ &= ZW'(Z)/W'(1) = \frac{(1 - q)^3(1 + qZ)Z}{(1 + q)(1 - qZ)^3} \end{aligned} \tag{B8}$$

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* β is equivalent to p'_A in Appendix A and since in the primary chain distribution we do not consider monomers obtained by splitting the AA monomer or splitting off a pendent double bond, the form of distribution considered here is to be related to the modified number fraction distribution given by equation (A2)

$$F_0(z, Z) = \sum n_{p-k,k}(p'_A Z_A z + p'_B Z_B)^{p-k} Z_S^k \tag{A2'}$$

Here, $N'(Z) = \delta N(Z)/\delta Z$ and $N'(1) = N'(Z = 1)$; the same rule applies to $W'(Z)$ and $Z(Z)$, thus

$$P_n^0 = N'(1) = 1/(1-q) \tag{B9}$$

$$P_w^0 = W'(1) = 1(1+q)/(1-q) \tag{B10}$$

$$P_z^0 = Z'(1) = (1+4q+q^2)/(1-q^2) \tag{B11}$$

giving for polydispersities

$$P_w^0/P_n^0 = 1+q, \qquad P_z^0/P_w^0 = (1+4q+q^2)/(1+q)^2 \tag{B12}$$

and in the limit of $q \to 1$

$$P_w^0/P_n^0 = 2, \qquad P_z^0/P_w^0 = 3/2 \tag{B13}$$