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Free-Radical Synthesis of Block Copolymers on an Industrial Scale

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Summary: Controlled free-radical polymerization has been monitored with great interest in recent years since it offers an opportunity to combine the advantages of conventional free-radical polymerization with those of living ionic polymerization. We present the 1,1-diphenylethene (DPE) method which enables us to produce block copolymers on an industrial scale by a free-radical mechanism.

This DPE process enables industrially relevant monomers, such as styrene, methacrylates, acrylates, methacrylic acid, acrylic acid and N-vinyl compounds, to be converted into block copolymers. The synthesis can be carried out in organic solvents, without solvents or in water.

We have been able to demonstrate, that the addition of 1,1-diphenylethylene to a normal free-radical polymerization results in polymers whose molar mass, after a short uncontrolled phase, increases in a linear manner with conversion. The amount of 1,1-diphenylethylene added also determines the order of magnitude of the final molar mass. It was also possible to employ the polymers isolated during this polymerization as initiators for the polymerization of a further monomer, resulting in the formation of block copolymers.

With possibly somewhat reduced claims on the perfection of the structures, a wide variety of possibilities arise with the known advantages of free-radical polymerization.

The one-pot synthesis is carried out by simple successive addition of the desired monomers and has already been used successfully on an industrially relevant scale.

Introduction

Until recently polymerizations with a high degree of structure control were only possible by means of relatively complex methods, such as anionic, cationic or group-transfer polymerization. But these methods have the disadvantage that the high structure control is balanced by a limited choice of monomers and the high sensitivity of the reaction to impurities. Conventional free-radical polymerization on the other hand is a relatively insensitive process with high tolerance to functional groups, but without the possibility of structure control.

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Controlled free-radical polymerization combines the advantages of ionic and free-radical polymerization: a wide range of monomers with a high degree of structure control. It is ideally insensitive and can be carried out in existing plants.

The high structure control facilitated by controlled free-radical polymerization is of course not an end in itself, but has three industrial benefits:

1. The synthesis of gradient, block or comb polymers instead of random copolymers enables the production of materials with new or improved properties which are suitable, for example, as dispersants and emulsifiers, as thickeners, impact modifiers, phase promoters or adhesives. The low polydispersity in these cases is of minor concern.
2. On the other hand, low polydispersity of block copolymers or even homopolymers may be important for applications in pharmacology or powder coatings.
3. In functional polymers, expensive monomers which are the actual active component can be partially replaced by a less expensive monomer without impairing the effectiveness of the product.

We would like to pick out one of these potential areas of application of block copolymers, namely dispersants, in order to underscore the economic importance.
In 1995 600,000 metric tons of dispersants were produced in the USA, somewhat more than half of which were polymers. In 2000 it was almost 700,000 metric tons of dispersants. The value of polymeric dispersants produced in the USA in 1995 was almost $500 million, in 2000 it was more than $600 million.
Extrapolated to world production of polymers, this means that polymeric dispersants with a value of around $2.1 billion were produced worldwide in the year 2000.

The first steps toward controlled free-radical polymerization were taken in the 1970′s. Borsig and Braun polymerized MMA with diaryl- and triaryl-containing protecting groups.[1] They observed an increase in the molecular weight with conversion and the formation of block copolymers. Minoura polymerized MMA in the presence of chromium(II)acetate and again observed an increase in the molecular weight with conversion and the formation of block copolymers. [2]
In the 1980′s, Otsu used dithiocarbamates as iniferters in the polymerization. He derived the term iniferters from the term inifer used in cationic polymerization. He also

used the term “living free-radical polymerization” for the first time.[3] The first controlled free-radical polymerization with a stable free radical appeared in the patent literature: Rizzardo and Solomon reported polymerization with an AIBN/TEMPO adduct.[4] However, the implications of this patent were not recognized and it was forgotten. Rizzardo did not follow up this concept and used a different mechanism: the RAFT mechanism.[5]

In the 1990´s, eight years after the appearance of the Rizzardo and Solomon patent, controlled free-radical polymerization with stable free radicals was rediscovered by Georges. He published the controlled free-radical polymerization of styrene with TEMPO.[6] Matyjaszewski investigated the degenerative transfer of alkyl iodides for controlled free-radical polymerization.[7]

Also in the 1990s, Sawamoto and Matyjaszewski and other authors reported the controlled free-radical polymerization by ATRP with different metals, such as copper, ruthenium, iron, nickel and rhodium.[8-15]

The DPE Method

We have found that 1,1-diphenylethene is an additive, which also enables control of free-radical polymerization.[16-19] In a typical synthesis of the first block, the monomer, initiator and 1,1-diphenylethene are heated at 60 to 110°C for 2 to 12 hours. A second monomer is then added, and the mixture is heated at 60 to 110°C for a further 6 to 12 hours. Depending on the choice of monomer, this gives hydrophobic, amphiphilic or water-soluble block copolymers in a one-pot synthesis.

The DPE method is surprisingly flexible with respect to the choice of monomers and the solvent. The method works with all common monomers, which are capable of free-radical homopolymerization or copolymerization, even N-vinyl compounds and vinyl acetate. The polymerization can be carried out in organic solvents, in water or without a solvent. The reaction conditions are the usual ones for conventional free-radical polymerization, which is very beneficial for industrial implementation of the DPE method. The products are colorless and odorless with molecular weights from 5000 to 500,000 g/mol, and have typical block copolymer behavior.

Using methyl methacrylate and n-butyl acrylate, we have produced block copolymers with various block length ratios and molecular weights of up to 500,000 g/mol. For example, materials are obtained which are tacky in the case of long n-butyl acrylate blocks and highly elastic in the case of long methyl methacrylate blocks.

Methyl methacrylate and styrene can be converted into block copolymers by the DPE method. The right curve in the GPC in figure 1 shows the first block of homomethyl methacrylate, and the left curve shows the block copolymer after reaction of the first block with styrene. It is clear from the curves that the polydispersity is higher than in other methods of controlled free-radical polymerization.

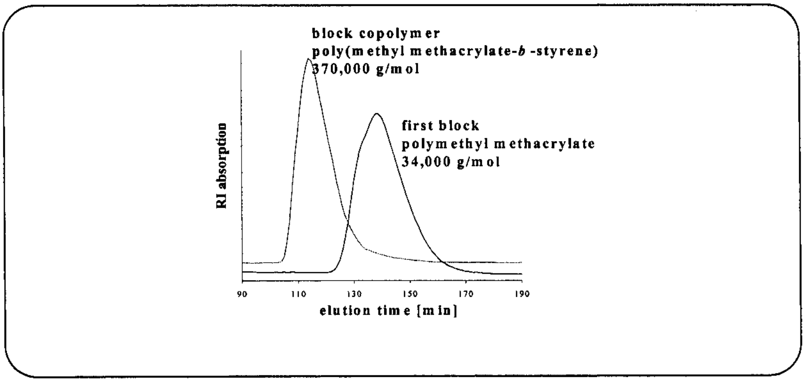
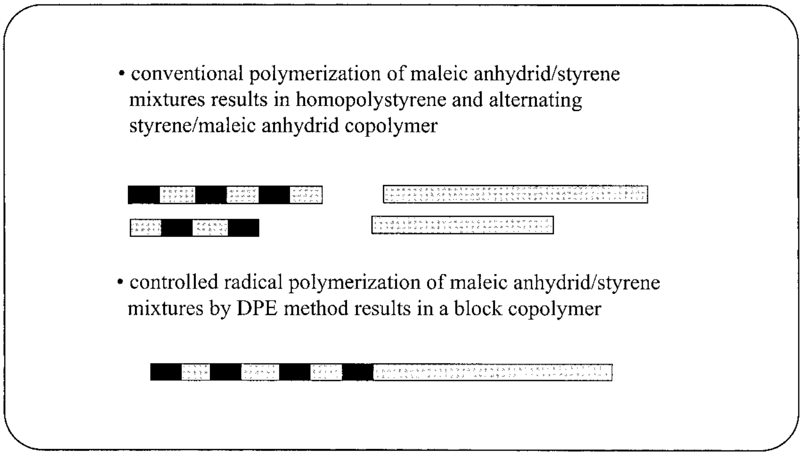


Figure 1: GPC curves of poly(methyl methacrylate), M_w = 34,000 g/mol, and the block copolymer poly(methyl methacrylate-*b*-styrene), M_w = 370,000 g/mol, obtained from it by the DPE method.

The DPE method also enables the production of block copolymers from styrene and maleic anhydride (MSA) (Figure 2). The conventional free-radical copolymerization of styrene and maleic anhydride gives a mixture of alternating maleic anhydride/styrene copolymer and homopolystyrene if styrene is present in excess. In the presence of 1,1-diphenylethene, however, the termination reaction can be suppressed and a pure styrene block is polymerized onto the first block of alternating styrene and maleic anhydride. This enables an amphiphilic block copolymer with novel interesting properties to be obtained from inexpensive monomers in a one-step one-pot synthesis.



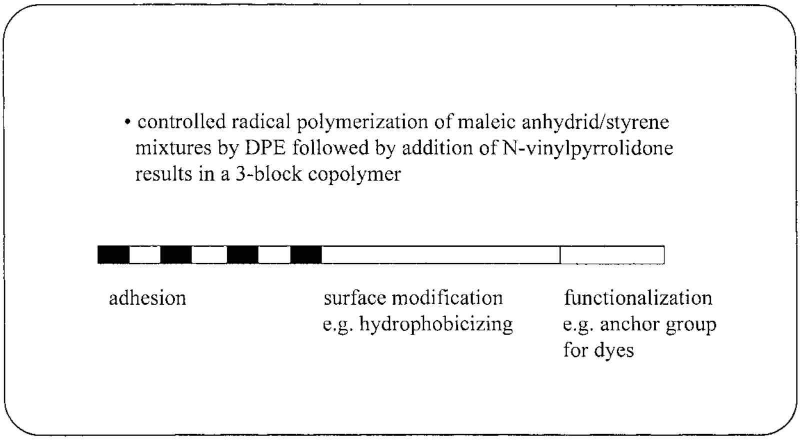
- conventional polymerization of maleic anhydrid/styrene mixtures results in homopolystyrene and alternating styrene/maleic anhydrid copolymer
- controlled radical polymerization of maleic anhydrid/styrene mixtures by DPE method results in a block copolymer

Figure 2: Styrene/MSA block copolymers by the DPE method.

Table 1: Hydrophobic surface modification with polymers obtained from styrene/MSA mixtures, copolymerized conventionally and with the DPE method.

	contact angle [^{O}] on	
	glass	paper
uncoated	65	12
styrene/maleic anhydride, copolymerized **without** diphenylethene poly(styrene-*alt*-maleic anhydride)/polystyrene mixture	106	65
styrene/maleic anhydride, copolymerized **with** diphenylethene poly((styrene-*alt*-maleic anhydride)-*b*-styrene)	118	110

We have reacted a styrene/maleic anhydride mixture with DPE to give an amphiphilic block copolymer and polymerized a styrene/maleic anhydride mixture with the same monomer ratio by a conventional method without DPE (Table 1). In a very simple experiment glass and paper were coated with these products and the contact angle of the surfaces was measured. The expected hydrophobicizing effect is evident in all cases. However, the effect is much stronger in the case of the block copolymer and the difference is greater the more polar the coated surface. The polar block interacts with the polar surface, causing the hydrophobic polystyrene blocks of the block copolymer to point away from the coated surface like a brush. If the polar and non-polar blocks are not chemically bonded, but are merely in the form of a physical mixture, as in the case of the styrene/maleic anhydride mixture polymerized without DPE, this self-orientation cannot occur, as impressively confirmed by the experiment.



- controlled radical polymerization of maleic anhydrid/styrene mixtures by DPE followed by addition of N-vinylpyrrolidone results in a 3-block copolymer

Figure 3: Poly((styrene-*alt*-MSA)-*b*-styrene-*b*-N-vinylpyrrolidone) by the DPE method.

The DPE method also enables a further block, in this case a polyvinylpyrrolidone block, to be polymerized onto a styrene-maleic anhydride block copolymer (Figure 3). Each block in this 3-block copolymer does a particular job: the block comprising alternating styrene and maleic anhydride causes adhesion through interaction with a polar surface, the styrene block renders the surface hydrophobic, and the polyvinylpyrrolidone block, owing to its complexing ability, is particularly suitable as anchor group, for example for dye molecules.

We have been able to produce other very interesting block copolymers using the DPE method. N-vinylpyrrolidone and styrene give amphiphilic block copolymers in various block length ratios. Depending on the block length ratio, the products are colloidally soluble, dispersible or only swellable in water. They have a strong complexing tendency, for example for oil and iodine, and the thickening effect which is typical of block copolymers. The electron photomicrograph (Figure 4) shows the continuous black styrene phase and the discontinuous pale N-vinylpyrrolidone phase. The N-vinylpyrrolidone/styrene block length ratio is 30/70.

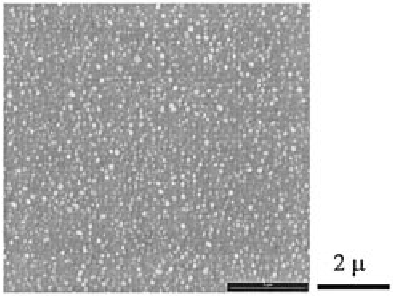


Figure 4: Electron photomicrograph of poly(styrene-*b*-N-vinylpyrrolidone) block copolymer obtained by the DPE method. The N-vinylpyrrolidone/styrene block length ratio is 30/70. The continuous black phase shows styrene and the discontinuous pale phase N-vinylpyrrolidone.

The DPE method can also be used to produce block copolymers from ethene and styrene. To this end, a DPE-containing polystyrene was reacted with ethene at 1300 bar and 250°C in an industrial plant, and a block copolymer was obtained in a exothermic reaction. Block copolymers of this type may be of great economic importance.

Demonstration of Block Structure

We have used various methods to demonstrate the block structure of the copolymers obtained by the DPE method.

Strong indications of the formation of block copolymers were firstly the observed monomer conversion and an increase in the molecular weight in the second step. The solubility behavior of amphiphilic block copolymers is characteristic and was also found in the copolymers produced by the DPE method: the addition of organic solvents gives opaque solutions or dispersions which suddenly became clear on addition of, for example, small amounts of water. GPC-IR coupling confirms the presence of block copolymers from the parallel intensities of the absorption in the GPC and in the IR at a wavenumber that is characteristic of one of the monomers. Pyrolysis GC-MS coupling clearly showed the presence of fragments consisting of two different chemically linked monomer types. We have also carried out extraction experiments and recorded electron photomicrographs, which we would like to explain in somewhat greater detail.

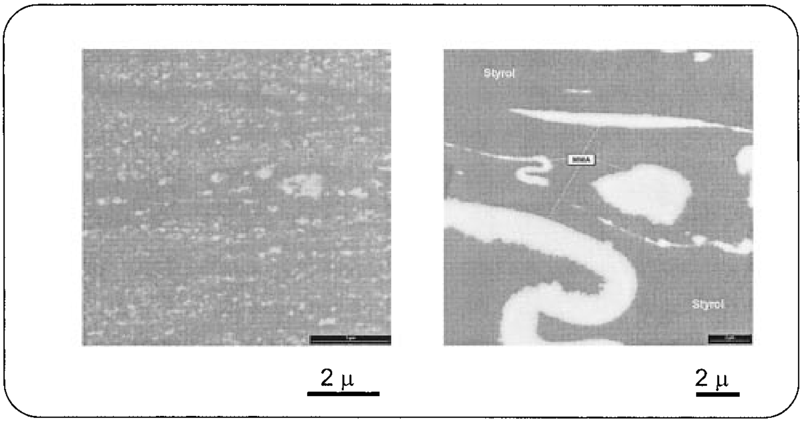


Figure 5: Electron microscopy picture of block copolymer of methyl methacrylate and styrene obtained by the DPE method (left) and of a mixture of polystyrene and polymethyl methacrylate (right). The molecular weights and mixing ratios are comparable.

In order to demonstrate that block copolymers really can be obtained by the DPE method, electron photomicrographs were recorded (Figure 5). On the left-hand side one can see the electron photomicrograph of a block copolymer of methyl methacrylate and styrene produced by the DPE method. On the right-hand side is the electron photomicrograph of a physical mixture of homopolystyrene and homopolymethyl methacrylate. The molecular weights and mixing ratios are comparable. Owing to incompatibility, the two polymers separate in the right-hand picture and form large domains. The styrene phase appears black and the methyl methacrylate phase white. In the left-hand picture, by contrast, there appears to be a separation on a smale scale in spite of the incompatibility as it is typical for block copolymers. The different polymer blocks must be chemically linked, i.e. a block copolymer is present.

Further evidence of the block structure in the copolymers produced by the DPE method was provided by extraction experiments (Figure 6). To this end, a block copolymer of methyl methacrylate and styrene produced by the DPE method was extracted with cyclohexane in a Soxhlet apparatus. Cyclohexane is a solvent for homopolystyrene, but not for homopolymethyl methacrylate. After the extraction, an IR spectrum of the residue was recorded.

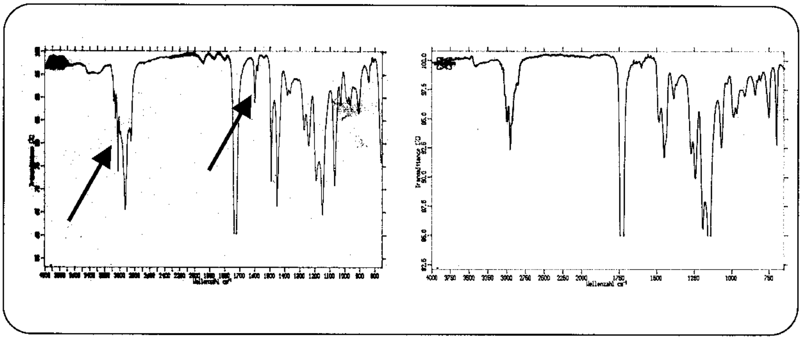


Figure 6: IR-Spectra of block copolymer of methyl methacrylate and styrene obtained by the DPE method (left) and of a mixture of polystyrene and polymethyl methacrylate (right) after extraction with hot cyclohexane. The molecular weights and mixing ratios are comparable. Arrows indicate styrene signals.

The IR spectrum on the left-hand side clearly shows the styrene signals (see arrows) in spite of the preceding cyclohexane extraction. The right-hand picture shows the IR spectrum of the residue of the physical mixture of homopolystyrene and homopolymethyl methacrylate which has been subjected to the same extraction with cyclohexane in a Soxhlet apparatus. The molecular weights and mixing ratios are comparable. The IR spectrum no longer contains a signal for styrene. This means that a block copolymer really must be present in the case of the copolymer produced by the DPE method.

We have recorded an electron photomicrograph of a 3-block copolymer of n-butyl acrylate, styrene and n-butyl acrylate in order to demonstrate the presence of a block copolymer (Figure 7). The black, continuous phase shows the styrene phase, and the white, discontinuous phase shows the n-butyl acrylate phase. This is a block copolymer with a molecular weight of around 370,000 g/mol and a polydispersity of 2.6. As already mentioned, the block copolymers synthesized by the DPE method are not distinguished by particularly low polydispersity. This also means that although the electron photomicrographs show the small domains that are typical of block copolymers, they do not show the usual high degree of order.

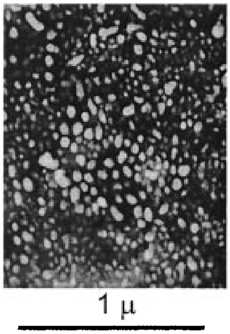


Figure 7: Electron microscopy picture of a A-B-A 3-block copolymer of n-butyl acrylate, styrene and n-butyl acrylate (M_w = 366,000 g/mol, M_w/M_n = 2.6), stained with RuO_4.

Block Copolymers from Anionically Polymerized DPE Copolymers

"Super Polystyrene", a former research product of BASF, is a copolymer of styrene and 1,1-diphenylethene (Figure 8), which has a higher glass transition temperature than pure polystyrene. The glass transition temperature increases with the DPE content. It is synthesized by anionic copolymerization.

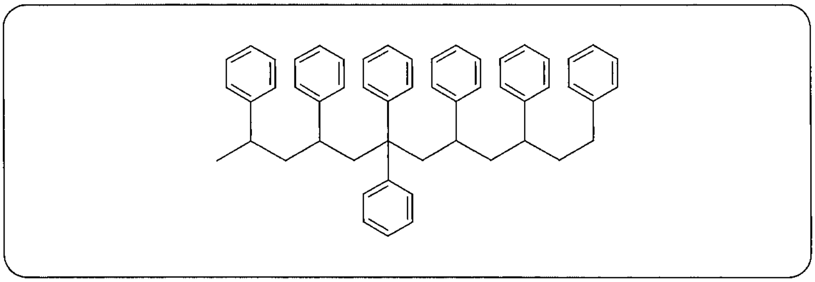


Figure 8: Structure of anionically polymerized styrene-DPE copolymer.

Against the background that polymers containing DPE can be reacted with a further monomer by a free-radical mechanism to give block copolymers, it was interesting whether it is possible for a "super polystyrene" of this type to be reacted with a monomer which is capable of free-radical polymerization to give block copolymers. In fact, by simply warming a "super polystyrene" with a molecular weight of 180,000 g/mol with a monomer that is capable of free-radical polymerization, in this case methyl methacrylate, we have obtained a corresponding block copolymer with a molecular weight of 215,000 g/mol. For it a copolymer, containing 90 % styrene and 10 % 1,1-diphenylethene was dissolved in methylmethacrylate and heated up to 105 ^{O}C for 8 h.

The DPE Mechanism

The mechanism of the DPE method is not yet clear. We have indications which make various mechanisms appear plausible. It is also possible for more than one mechanism to take place, perhaps depending on the monomer.

The mechanism shown in figure 9 is, that the growing polymer chain can be blocked reversibly with a DPE molecule, and so enables the successive incorporation of various monomers. An irreversible head-to-head termination of the polymeric free radicals can take place as a side reaction. It is also possible for the diphenylethyl-terminated polymeric free radicals to combine. However, this should result in a highly substituted ethane bond, which, as it is thermally labile, can be broken again and finally can release the polymeric free radical again.

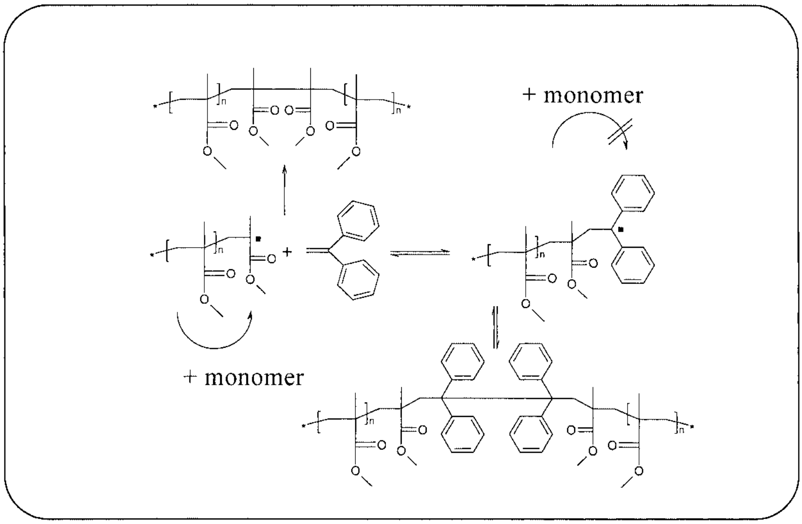


Figure 9: DPE mechanism 1.

Another possible mechanism is for 1,1-diphenylethene to be incorporated into the polymer chain or to retard the growth of a polymer chain and finally to combine with a further growing polymer chain in a head-to-head termination reaction (Figure 10). Both cases result in a polymer structure which includes a 1,1-diphenylethyl unit as a sort of predetermined breaking point. In a second step (Figure 11), the diphenylethyl unit in the para-position is attacked by a free radical and finally reversibly liberates a polymeric free radical, which is able to adduct a further monomer and so results in block copolymers. The driving force for this reaction could be the formation of a quinoid structure with the associated extension of the delocalized π system of 6 from 12 electrons. A point in favor of this assumption is that the block copolymer formation can be considerably accelerated by the continuous addition of small amounts of initiator.

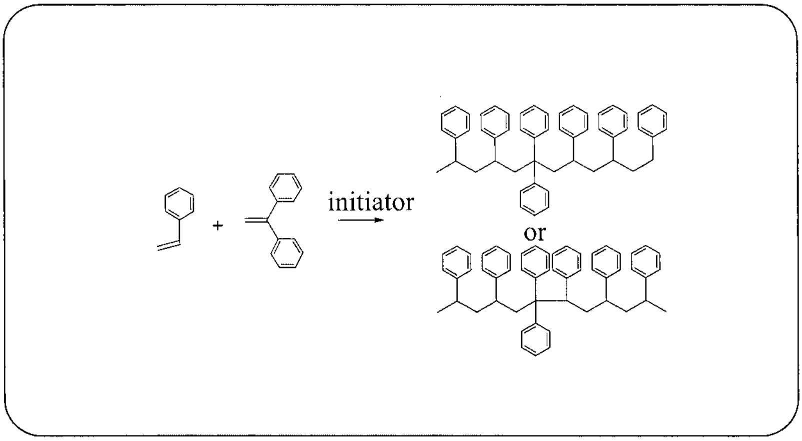


Figure 10: DPE mechanism 2, first step.

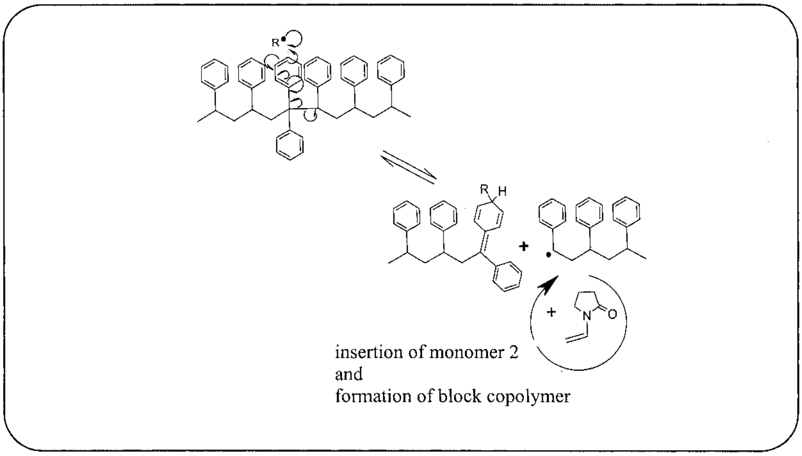


Figure 11: DPE mechanism 2, second step.

A further mechanism which appears plausible is based on addition of 1,1-diphenylethene onto the growing polymer chain during polymerization of the first block (Figure 12). After a temporary retardation of the polymerization process, a polymer-substituted diphenylethene and a new polymeric free radical are formed in a transfer reaction. The polymeric free radicals formed in this way react with further monomer and DPE until the latter have been consumed. The polymer-substituted DPE can then reversibly add a further polymeric free radical or liberate the original polymeric substituents in the form of a polymeric free radical (Figure 13). One or other of the polymeric free radicals are liberated alternately in this equilibrium reaction and is able to adduct a further monomer. At the same time, the concentration of free polymeric free radicals is suppressed to the extent that the combination reaction plays only a secondary role, but the desired polymerization reaction continues to occur.

In a side reaction, the diphenylethyl free radical substituted by two polymer chains can be converted into a diphenylethene derivative substituted by two polymer chains, with elimination or transfer of a hydrogen free radical, enabling the reaction to gradually subside. A further point in favor of this assumption is that the block copolymer formation can be considerably accelerated by the continuous addition of small amounts of initiator. In addition, the corresponding double bonds are detected in the ^{13}C-NMR.

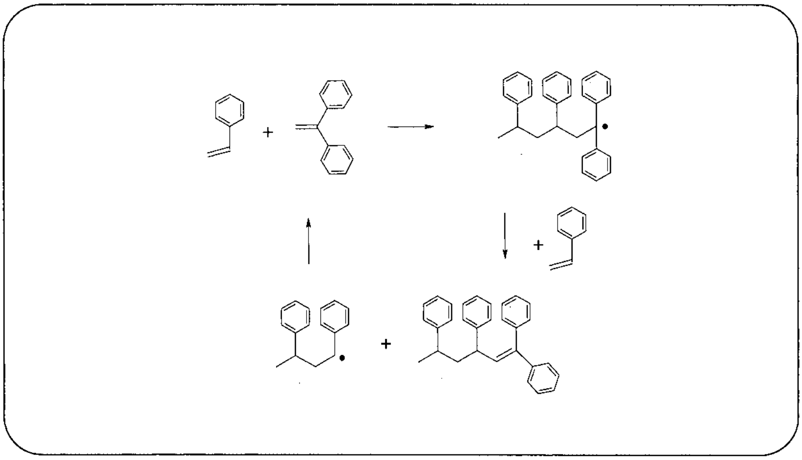


Figure 12: DPE mechanism 3, first step

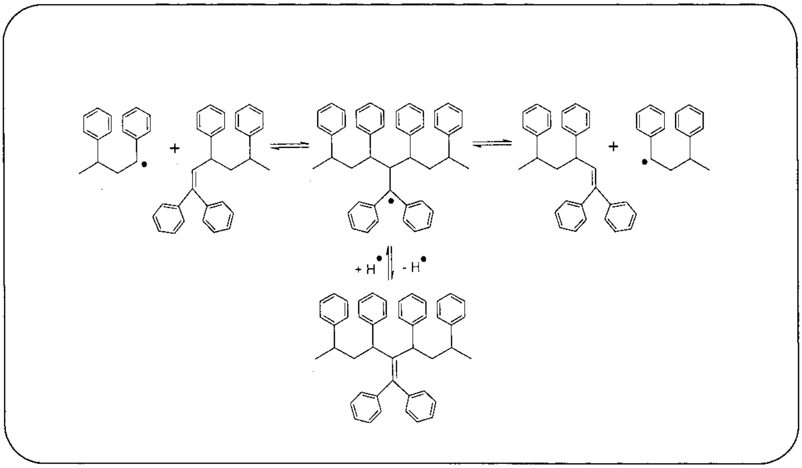


Figure 13: DPE mechanism 3, second step

The DPE method appears to be more versatile than other methods with respect to the choice of monomer. The fields highlighted in figure 14 show example structures which would reasonably be expected in the controlled free-radical polymerization of, for example, N-vinylpyrrolidone using the TEMPO or ATRP method. Either mixed N,O-acetals or geminal N-halogen compounds are formed here. However, both structures are very sensitive to elimination reactions and other side reactions at the reaction temperatures necessary for the respective reaction mechanism. The DPE method circumvents these problems since there are no heteroatoms to form structures which would facilitate the side reactions mentioned. This applies to all possible DPE mechanisms mentioned.

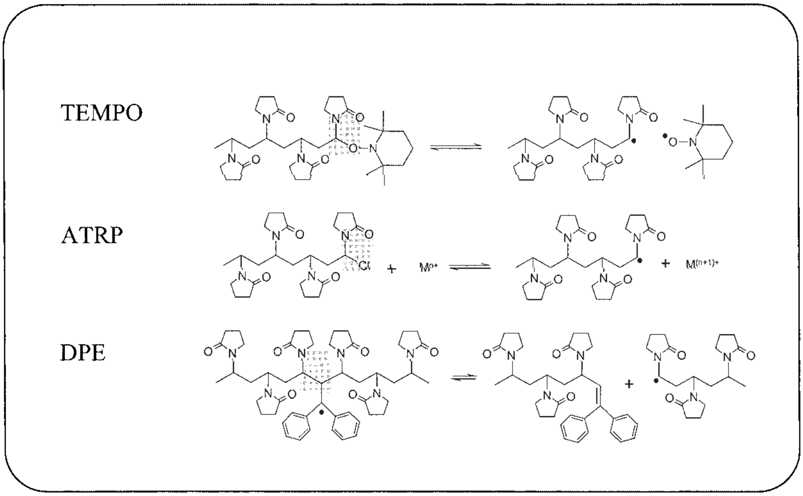


Figure 14: Versatility of the DPE-method

Conclusion

The DPE method enables the free-radical synthesis of block copolymers from all common free-radical homopolymerizable or copolymerizable monomers in organic solvents, water or without a solvent.

We have used the method to produce new materials, for example poly(N-vinylpyrrolidone-b-styrene), poly(N-vinylpyrrolidone-b-vinylacetate) and poly(styrene-b-ethene). In addition, the products are colorless, odorless and free from toxic additives. This is particularly important with regard to commercial applicability. The method is not suitable for the synthesis of polymers of low polydispersity. M_w/M_n is frequently between 2 and 3 and the materials produced in this way may contain a certain portion of homopolymer. However, both are negligible for many industrial applications. The DPE method does not compete with the known methods for controlled free-radical polymerization, but instead is intended to supplement the range of tools available to the polymer chemist. It is indisputable that all methods have their advantages and disadvantages. The mechanism is still unclear. We have indications which make one or other mechanism appear plausible, but as yet not all observations are consistent with a single mechanism alone. The most important factor is, however, that the DPE method enables us to produce block copolymers on an industrial scale, i.e. by the ton.

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