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Controlled Free Radical Polymerization

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Precise control of macromolecular structure and architecture continues to be a dominant theme of contemporary polymer research. Amongst the armoury of polymerization techniques available to polymer chemists, free radical polymerization is the oldest, most studied and extensively exploited in commercial practice. Nevertheless, free radical polymerizations have been most difficult to control and are generally characterized by broad molecular weight distribution, poor control of molecular weights and chain end functionality and inability to synthesize well-defined block copolymers.However, polymer chemists have, in recent years, succeeded in effectively controlling the free radical polymerization by invoking the concept of reversible termination involving an active species in rapid equilibrium with a dormant species. Using controlled free radical polymerization it is feasible to produce poly(styrene)s with polydispersities as low as 1.05 with good control of molecular weight. Furthermore, a variety of novel end functionalized polymers as well as random, block, graft, star and hyperbranched polymers have been prepared using controlled free radical polymerization. The paper reviews the explosive developments in this area since the appearance of the first publication in 1993. The scope of this new technique for polymer synthesis is illustrated with representative examples.

Introduction

Precise control of macromolecular structure and architecture continues to be a dominant theme of contemporary polymer research[1]. Fundamental to this endeavour is the availability of synthetic methods capable of providing a high degree of control on the primary bond making and bond breaking events that determine the course of a polymerization reaction, namely, chain initiation, propagation, transfer and termination[2]. Ideally speaking, after the chains are initiated, the chains should only continue to propagate without undergoing any chain breaking events such as transfer or termination process. Under these ideal conditions, the polymer growth reaction can be termed as highly "chemoselective", wherein the growing active center adds only to another monomer. High chemoselectivity in polymerization defines the size of the macromolecule, the uniformity of molecular weight and determines the ability to manipulate the terminal end of the polymer chain. If initiation is fast, then the degree of polymerization is uniquely defined by the ratio of the concentration of reacted monomer to that of the added initiator, namely, $DP_n = [M]/[I_o]$. Such a chemoselective polymerization has been called living polymerization in polymer science alluding to the existence of a reactive chain end during the course of the polymerization.

Living Anionic Polymerizations

Living polymerizations were first experimentally observed in chain reactions involving a carbanion as the growing end (anionic polymerization)[3]. Under conditions, wherein adventitious impurities are rigorously excluded, a carbanion chain end undergoes only propagation reaction with the complete absence of any termination or transfer process. In these systems, chain ends also do not react with one another due to electrostatic repulsions. Various ideal living systems have been described for alkenes and dienes polymerization as well as for ring opening polymerization of epoxides. Although less satisfactory, they have been extended to even more difficult systems such as polymerization of methacrylates (enolate chain ends)[4] and metathesis polymerization (metal-

locarbene chain ends)[5]. The living anionic polymerization systems have been recently reviewed[6].

Controlled Cationic Polymerization

Extension of these concepts to a cationic chain end (carbocationic polymerization) proved difficult. Spontaneous and facile elimination of hydrogen (as proton) from the β-carbon of the growing carbocation was thought to be a formidable obstacle to achieve livingness in cationic polymerization. However, the progress in better understanding of the behaviour of carbocations and the correct choice of experimental conditions led to better degree of control. The logic of the approach rested on the following premise. Kinetically, at high initiator concentrations ($[I_o] \geq 10^{-2}$ mol L^{-1}) the occurrence of transfer due to β- hydrogen elimination is not very prominent. Therefore, if initiation is fast, it is still possible to avoid or minimize the transfer reaction using a high initiator concentration. However, carbocations are very reactive towards alkene ($R_P \sim 10^5$ mol^{-1} L s^{-1} at ~ 20°C) and hence at high concentration of initiator (high carbocation concentration), the polymerization reaction will be uncontrollable. In order to reduce the rate of polymerization, it was proposed that the active carbocation should be in equilibrium with a dormant species with a fast and reversible equilibrium between the two species. Under such conditions, the number of chains (and hence $\overline{M}n$) will be determined by the total concentration of active and dormant species whereas the rate of polymerization will be proportional to the low concentration of the active species in equilibrium ($[C^*] \sim 10^{-7}$ mol L^{-1})[7].

Experimental conditions were defined for the controlled polymerization of styrene, isobutyl vinylether and isobutylene using cationic initiators[8]. These polymerizations are not ideally living since they possess a finite transfer and termination rate. But by appropriate choice of reaction conditions, their contributions to the polymer growth reaction can be minimized. Nevertheless, from a practical point of view the controlled polymerization is still useful in the sense that it can produce polymers with predetermined molecular weights, low polydispersity and controlled functionality. Furthermore, if after the consumption of the first monomer (A), a second monomer (B) is added, the polymerization will reinitiate again leading to a block copolymer of the type $(A\text{-}A\text{-}A)_m$ $(B\text{-}B\text{-}B)_n$.

Controlled Free Radical Polymerization

If, on the contrary, the growing chain ends are free radicals, there are two potentially damaging reactions, which render the possibility of a living radical polymerization still more difficult.. These are radical coupling and disproportionation. Of the two, fast termination of chain end by radical coupling is the most important chain breaking event in free radical polymerization. The importance of radical coupling increases with the concentration of growing species since termination is second order with respect to growing radical whereas propagation is first order. Thus the proportion of deactivated chains (dead chains) increases with increasing chain length. Furthermore, radical polymerization is characterized by slow initiation (and hence low stationary concentration of growing radical) and fast propagation.

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In view of these considerations, attempts to achieve controlled free radical polymerization of monomers were largely unsuccessful in the past. However, it was recognized that free radical polymerization is one of the most important commercial process for the synthesis of a host of useful materials. The number of monomers amenable to free radical polymerization is potentially large. Also, free radical polymerization occurs at 25 to 100° C and most often in water, as suspension, solution or emulsion. This is in contrast to ionic polymerization which often requires expensive organic solvents, complete exclusion of moisture and oxygen (< 10 ppm) and temperatures lower than ambient. Therefore, there exists strong motivation for extending the concept of living and controlled polymerization from ionic to radical process. This would enable synthesis of new materials with novel characteristics (functional polymers, block, graft and branched polymers/copolymers) from the readily available monomers using less expensive reaction conditions.

The most promising approach was to extend the principles underlying the controlled carbocationic polymerization to free radical polymerization. Thus, a method was sought by which one could ensure a low momentary or stationary concentration of growing radicals in solution. In other words, the objective was to render the radical less free. Furthermore, to ensure narrow polydispersity, the rate of initiation should be at least equal to or greater than the rate of propagation. However, there is one major difference between polymerizations propagating through carbocations and free radicals. Addition of the latter to a double bond is far too slow compared to the former; and if one considers the low stationary concentration of the growing radical, it can be anticipated that the controlled radical polymerization will be too slow for any practical applications. Based on the estimate of k_p and k_t at 60°C, it can be estimated that for styrene at $[M]_o$ = 1 mol L^{-1} and for synthesizing a polymer with a DP_n = 100, it will take more than one year to reach 99% conversion, if the stationary concentration of growing radicals is assumed to be 10^{-9} mol L^{-1} !

Nevertheless, the situation is not so hopeless. The rates of polymerization can be improved by accepting lower conversions, some finite termination of the growing radicals and by operating at higher monomer concentrations (higher stationary concentration of radicals). Polymerization at higher temperature has a favourable effect on ratio k_p/k_t, since the activation energy for propagation is always higher than that of termination. The choice of the monomer is also a factor to be reckoned with. The k_p/k_t ratio increases in the order ethylene (0.0005×10^{-4}) < styrene (0.03×10^{-4}) < methyl methacrylate (0.2×10^{-4}) < vinyl acetate (10^{-4}) < methyl acrylate (2.1×10^{-4}). Thus, with methyl acrylate one can operate at 70-times higher stationary concentration of growing radicals compared to styrene on account of the more favourable k_p/k_t ratio[9].

Based on the above kinetic frame-work, it is possible to understand the burgeoning literature on controlled free radical polymerization of vinyl monomers. Essentially literature uses two major approaches to ensure low stationary concentration of growing radical. One, use of a radical scavenger which would reversibly combine with a growing radical, but by itself would not add to the double bond and second, use a suitable transition metal compound which could reversibly complex with a growing radical and provide the necessary dormant species in equilibrium with the growing radical[10].

One of the first examples of a controlled polymerization of vinyl monomer using free radical chemistry is due to Otsu and Yashida[11] have shown that certain compounds (e.g. tetramethylthiuram disulfide) when heated, fragment to form two dithiocarbomate radicals which act both as primary radicals to initiate polymerization and as also radical chain transfer agents and terminators (iniferters). Chain growth results from the repeated breaking of the polymer chain dithiocarbamate bond, addition of monomer followed by termination by the dithiocarbamate radical. Molecular weight increased in a linear fashion with reaction period and conversion. This result can be contrasted with a conventional free radical polymerization process in which high molecular weight is obtained early in the reaction and remains more or less constant until the gel effect occurs[12]. The polymerization obeys a first order kinetics in monomer as often observed for stationary state kinetics. However, these reactions do not qualify for being termed as living or controlled since they neither produce narrow polydispersity nor permit synthesis of polymers with predetermined molecular weights. Nevertheless, Nair and Clouet[13] creatively

exploited this chemistry to make end functionalized polymers and diblock/multiblock copolymers by suitable choice of the iniferters. Many other initiators with features similar to those exhibited by iniferters have been reported in the literature. However, none of these reactions would rigorously satisfy all the criteria needed to qualify them as living or controlled polymerization.

Reversible Combination of Radicals with Stable Free Radicals

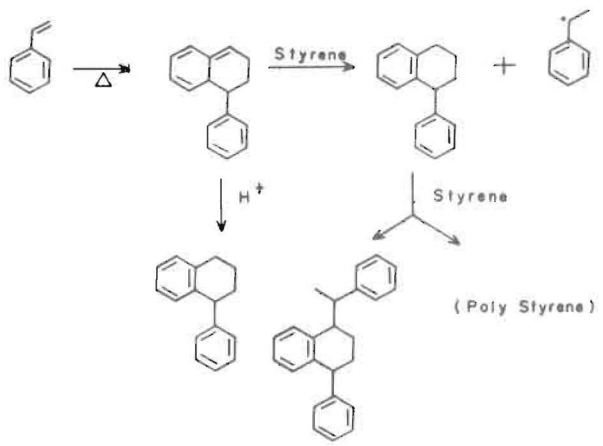
The first example of a controlled free radical polymerization using a stable free radical (SFR) as a radical scavenger to reversibly combine with a growing radical appeared in 1993 and is due to the work of Georges *et al.*[14] at Xerox Research Center, Canada. They used a nitroxide stable radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to form weak adducts in dynamic equilibrium with the growing styryl radical. The advantage of stable free radicals like TEMPO is that they themselves do not add to double bond. Using benzoyl peroxide (BPO) as initiators at 123°C, styrene was polymerized in bulk (TEMPO/BPO = 1.2) to give a 90% conversion to poly(styrene) after 70 hours with a $\overline{M}n$ = 7800 and $\overline{M}w$ = 10,000 and a $\overline{M}w/\overline{M}n$ = 1.27. $\overline{M}n$ increased linearly with time and conversion (up to 70%). Increasing TEMPO/BPO ratio to 3, resulted in reduced conversion and molecular weight. However, polydispersity values became narrower. The polymerization rate was first order in monomer concentration.

These results are indicative of a lower stationary concentration of the growing polystyryl radical in dynamic equilibrium with a thermally labile adduct of the polystyryl radical with TEMPO. Fortuitously, it was observed that addition of camphor sulfonic acid (CSA) caused a dramatic increase in the rate of polymerization as well as molecular weight[15]. There was a slight broadening of polydispersity. Typically, it was shown that heating a mixture of CSA (0.018g) with TEMPO (0.013g) and BPO (0.015g) in styrene (36g) at 127°C gave a poly(styrene) with $\overline{M}w$ = 147,412, $\overline{M}n$ = 107,556 and $\overline{M}w/\overline{M}n$ = 1.37. CSA, presumably, reduces the autopolymerization of styrene, which, competes with stable free radical mediated polymerization, leading to broadening of molecular weight distribution. More recently, 2-fluoro-1-methylpyridinium *p*-toluenesulfonate has been demonstrated to result in a greater enhancement of the rate of polymerization compared to CSA, without broadening the molecular weight distribution[16]. The mechanism of action of this compound is yet unclear.

The approach has been successfully applied not only to bulk homopolymerization and block copolymerization but also to suspension copolymerization and emulsion homopolymerization.

The feasibility of preparing a stable, isolable polystyrene end capped with a nitroxide stable free radical was demonstrated. It was shown that this dormant species upon heating with fresh styrene, undergoes chain extension with slight broadening of molecular weight distribution[17]. Such nitroxyl end capped polymers were considered as suitable precursors for the preparation of block copolymers.

One of the competing processes that needs to be considered while conducting a free radical initiated styrene polymerization at 140-150°C is the autopolymerization. Autopolymerization of styrene has been extensively studied and is believed to occur by the Mayo mechanism[18]. The primary step in this mechanism is the Diels-Alder type reaction between two styrene molecules leading to an intermediate which by a two electron transfer process generates the free radicals necessary for the initiation of polymerization (Scheme 1). It has been reported that strong acids (e.g. camphor sulfonic acid (CSA) can convert the Diels Alder product into the innocuous product and thus inhibit autopolymerization. Recent studies by Georges *et al.*[19] have shown that benzoic acid is a more potent inhibitor of autopolymerization.



Scheme 1 — Mechanism of autopolymerization of styrene

Autopolymerization of styrene at 130°C in the presence of TEMPO and benzoic acid gave after 39 h, poly(styrene) with $\overline{M}w$ 10326 and $\overline{M}n$ 7304 and $\overline{M}w/\overline{M}n$ = 1.41 (58% conversion). Under identical conditions but without benzoic acid poly(styrene) with $\overline{M}n$ = 1658, $\overline{M}w$ = 4289, $\overline{M}w/\overline{M}n$ = 2.58 (32% conversion) was obtained. Autopolymerization of styrene at 130° could be inhibited by benzoic acid up to 15 h.

Addition of CSA increases the molecular weight but also causes broadening of polydispersity. Peroxide initiated styrene polymerization gave the narrowest polydispersity. Thus, the choice of BPO as initiator turned out to be fortuitous since, benzoic acid is produced *in situ* during the thermal decomposition of BPO. The primary rate enhancement mechanism due to organic acids, such as CSA, in nitroxide mediated polymerizations is proposed to involve the consumption of nitroxide radicals. The resulting reduction in nitroxide concentration affects the equilibrium between growing and dormant chains, increasing the number of growing chains, and hence the polymerization rate[20].

However, conflicting results have been reported by Matyjaszewski and coworkers[10]. They showed that addition of 0.02 - 0.12 *M* TEMPO to bulk polymerization of styrene at 120°C, resulted in a linear plot of $\overline{M}n$ versus conversion. The reaction was characterized by an induction period which decreased with increasing TEMPO concentration. $\overline{M}n$ up to 10,000 with polydispersity of 1.2 - 1.3 could be achieved. Polydispersity tend to broaden with increasing conversion. Thus, narrow polydispersity resins could be obtained even in the absence of any acid additives. The amount of scavenger was reported to control polymerization rates and molecular weights.

Styrene polymerization can also be initiated by azo-bis- isobutyronitrile (AIBN) in the presence of TEMPO. However, rates of polymerization were slower than BPO[10].

Modification in the structure of the stable free radical has a significant effect on the course of AIBN initiated polymerization of styrene at 120°C. 4-Phosphonoxy-TEMPO produced higher rates and higher molecular weight compared to TEMPO whereas 4-hydroxy TEMPO depressed both rate and molecular weight[10]. Using a more complex coordinated nitroxides, styrene polymerization was reported even at 80°C. Under similar conditions polymerization of vinyl acetate, methyl acrylate and methyl methacrylate were faster than styrene (bulk, AIBN, 0.03 *M* : TEMPO, 0.03*M*).

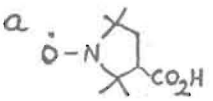
Nitroxide mediated stable free radical polymerization has been extended to the aqueous phase polymerization of sodium styrene sulfonate[21]. The polymerization was performed in 80% by volume aqueous ethylene glycol, using $K_2S_2O_8$/Na HSO_3 as the initiator ($[M]_o$ = 0.146 mol, $[I]_o$ = 6 m*M* $K_2S_2O_8$, 8 m*M* $NaHSO_3$, $[TEMPO]_o$ = 12 m*M* 120°C, 4h). The conversion to polymer was 96%, $\overline{M}n$ = 23000 and $\overline{M}w/\overline{M}n$ = 1.35. It was possible to isolate the nitroxide terminated poly(styrenesulfonic acid) ($\overline{M}n$ 8000, $\overline{M}w/\overline{M}n$ = 1.08) as a solid powder, which upon redissolving in an aqueous EG solution containing additional monomer reinitiated the polymerization. Thus, the chain end is not only living, it is also isolable and can be even stored!

It has been shown that the nitroxide mediated stable free radical polymerization does not show any gel or Tromsdorff effect because of the living nature of polymerization[22]. The mechanism of living free radical polymerization using nitroxide radicals indicate that the polymerization is first order in monomer concentration. Furthermore, the termination of polymer chains by radical combination is greatly reduced[23]. Results obtained with bulk polymerization of styrene using stable free radicals are summarized in Table 1.

Mardare *et al.*[24] reported that methyl methacrylate (MMA) could be polymerized in a controlled manner using an organoaluminum compound complexed with a stable free radical in the presence of a bidentate Lewis base. For example, use of triisobutyl aluminum in conjunction with TEMPO or TEMPO and bipyridyl caused a rapid polymerization of MMA at 25°C in benzene. The semilogarithmic time - conversion plot was linear, indicating a constant concentration of active species. However, only the tricomponent system showed a linear increase in $\overline{M}n$ conversion with a polydispersity of 1.25. The initiator efficiency (Ieff) was 0.68. A maximum $\overline{M}n$ = 15000 was reported under these conditions. A radical mechanism involving the growing PMMA radicals reversibly stabilized by a neutral tri or pentacoordinated aluminum derivative was proposed.

Table 1 — Bulk polymerization of styrene using TEMPO/BPO

Sl no.	Styrene, g (mol)	BPO, g (mmol)	TEMPO, g (mmol)	Acid, g (mmol)	Temp., °C	Time, h	% Conv.	$\overline{M}n\times10^{-3}$	$\overline{M}w\times10^{-3}$	$\overline{M}w/\overline{M}n$
1	36 (0.346)	0.015 (0.06)	0.013 (0.08)	Camphor sulfonic acid (0.018)	127	3	—	107.6	147.4	1.37
2	15 (0.144)	0.15 (0.06)	0.22[a] (1.2)	—	145	3.5	—	11.7	14.3	1.22
3	12 (0.115)	—	0.10 (0.64)	—	130	39	32	1.66	4.29	2.58
4	12 (0.115)	—	0.10 (0.64)	Benzoic acid 0.08 (0.66)	130	39	58	7.30	10.33	1.41
5	12 (0.115)	—	0.10 (0.64)	Camphor sulfonic acid 0.076 (0.32)	130	39	48	9.6	15.5	1.61
6	12 (0.115)	—	0.30 (1.9)	—	120	~24	~80	—	—	1.3

a 

A similar initiator system was also reported to be effective for the controlled polymerization of vinyl acetate[25]. A 1:1:2 complex of aluminum triisobutyl, 2,2′-bipyridyl and TEMPO was polymerized in benzene at 20 to 60°C for 12-24 h. The reaction was first order in monomer as shown by the linear time - conversion plot. Thus, the monomer is involved in the rate limiting step and indicates a constant concentration of active species. $\overline{M}n$ also increased linearly with time. These observations indicate that the initiation is rapid and transfer/termination reaction is minimal. From the kinetic data, the order with respect to initiator was found to be 0.3. The apparent activation energies were found be 6.7 kcal mol^{-1} which is higher than that for the free radical polymerization of vinyl acetate (Ea = 4.5 kcal mol^{-1}). The higher activation energy could be due to the combined contribution of activation energy for radical propagation and the enthalpy of the equilibrium between the active and the dormant species. The polymerization rate was strongly accelerated in the presence of two equivalents of TEMPO. At four equivalents, the reaction was completely inhibited. Using a vinyl acetate concentration of 2.5 M in benzene and a Al $(iBu)_3$-2,2-bipyridine-TEMPO (1:1:2) and initiator concentration of 0.05 M or 0.3 M at 20 or 60°C resulted in a polymer with $\overline{M}w/\overline{M}n < 1.3$ with marginal broadening of distribution with increasing conversion. $\overline{M}n$ up to 30,000 could be obtained.

These observations were rationalized based on a hexacoordinated aluminum bound to the bipy ligand and two molecules of TEMPO (dormant species) which is in equilibrium with an alkyl radical (active species) and a penta coordinated aluminum compound[25]. However, the $\overline{M}n$ vs per cent conversion plot and $\ln [M]_o/[M]$ vs time plot showed significant curvature, indicating that the concentration of active center was not constant throughout the reaction period. In the case of MMA, severe transfer reactions were observed. Polydispersity values were not reported. The limitation of stable free radical mediated

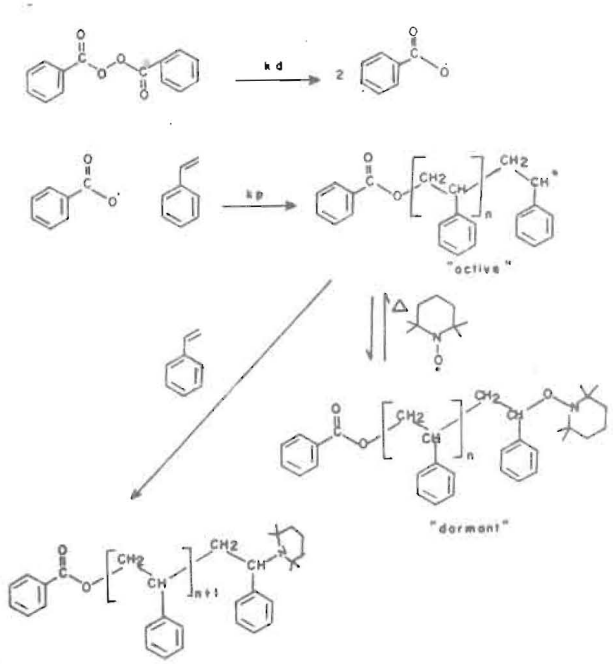
polymerization has been discussed[26]. Without providing experimental details, it is claimed that homopolymers of *n*- butylacrylate ($\overline{M}n$ ~ 15,000, $\overline{M}w/\overline{M}n$ = 1.5) and poly(styrene) ($\overline{M}n$ ~ 200,000 and $\overline{M}w/\overline{M}n$ = 1.3) as well as random block copolymers of styrene and *n*- butylacrylate (65% conversion, $\overline{M}n$ ~ 25,000 and $\overline{M}w/\overline{M}n$ = 1.5) can be prepared using nitroxide mediated polymerization.

The behaviour of stable free radical mediated controlled radical polymerization can be best understood based on a mechanism, involving fast initiation by radicals generated by TEMPO assisted decomposition of radical initiator followed by reversible trapping of the polystyryl radical by scavenging TEMPO to form dormant alkoxyamines. Alkoxyamines are thermally unstable at temperature > 120°C and can reversibly decompose, generating polystyryl radical and releasing TEMPO. Thus, irreversible termination by radical coupling is minimized. Because radicals are continuously generated, they will also react with the dormant alkoxyamines in a degenerative transfer process. The active and the dormant species exchange rapidly, resulting in linear growth of all chains with conversion and leading to polymers with narrow polydispersities (Scheme 2). The polydispersity in the bulk living free radical polymerization mediated by nitroxide is controlled by the exchange rate between the growing and dormant chains[27].

The TEMPO molecule attached to chain ends is extremely stable and is resistant to hydrolysis under all conventional polymer termination conditions. Even alkali treatment cannot hydrolyze the carbon-TEMPO bond! The only method currently available to eliminate the TEMPO molecule from the polymer chain end is by reaction of the polymer with a large excess of tri-n-butyltin hydride.

Reversible Complexation of Radicals with Organometallic Compounds

Carbon based radicals exhibit reversible complexation behaviour with several organo metallic compounds. Such complexes play an important role in biological systems as well as in synthetic organic chemistry for the formation of carbon - carbon bonds. Metal mediated radical reactions can promote many C-C bond forming reactions in organic chemistry with a high degree of regio - and stereoselectivity[28]. It is therefore not surprising that polymer chemists



Scheme 2 — Mechanism of styrene polymerization initiated by BPO in the presence of TEMPO

have attempted to exploit the potential of this method for controlled synthesis of polymers.

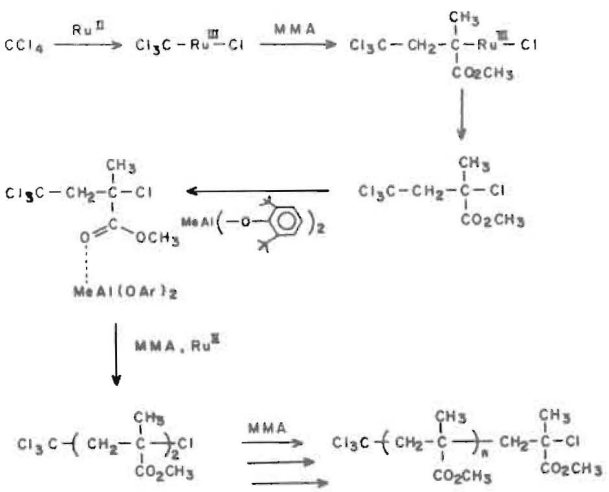
Aromatic diazonium salts decompose in the presence of metal complexes to yield radicals which initiate the polymerization of MMA with a reasonable degree of control using 5 *M* MMA in THF - acetone (1:1) at 40°C, various metal acetates (Ce, Co, Cr, Rh) were found to initiate polymerization using *p*- chlorobenzene diazonium tetraborofluorate. Ce $(OAc)_2$ gave the best results. The maximum $\overline{M}n$ that could be obtained was 30,000 after 6 h[29]. The polydispersity index was in the range of 1.5 - 1.8 in the conversion range of 20-80%. The polymer had a syndiotacticity of 65-70% as expected for conventional free radical polymerization. Under similar conditions, methyl acrylate gave uncontrolled polymerization.

Kato *et al.*[30] have recently reported that the Kharasch reaction can be used to initiate the controlled polymerization of MMA. The Kharasch reaction involves the addition of CCl_4 to an unsaturated double bond, giving the 1:1 adduct in high selectivity and yields. The reaction proceeds by a radical mechanism in which the transient radical is confined in the coordination sphere of a transition metal atom and thus remains stabilized. Many metals have been used for the promotion of Kharasch reaction . If the Kharasch

reaction can be induced to occur successively with additional monomer, then polymerization would occur. However, using conditions under which CCl_4 can be activated, C-Cl bond cannot be activated. However, in presence of a Lewis acid, methylaluminum bis-2,6-di-t-butyl phenoxide, [Me Al $(ODBP)_2$] at 60°C, 90% conversion was obtained in 4 h. The resulting PMMA had $\overline{M}n \sim 5200$ and polydispersity index of ~ 1.3. No polymerization was observed in the absence of either Ru or Al compound. The semilogarithmic plot of $\ln([Mo]/[M])$ vs time was linear indicating that the reaction was first order in monomer. The plot of $\overline{M}n$ vs conversion deviated from linearity beyond 25% conversion and became progressively lower than $\overline{M}n$ calculated, indicating the presence of distinct transfer reactions. Monomer resumption experiment indicated that the chain ends were quasi living in nature.

A free radical mechanism was inferred from these and other results. The proposed pathway involves an equilibrium between Cl terminated PMMA chain end (dormant) and a PMMA radical stabilized by the coordination with the ruthenium atom. The role of the Lewis acid is to coordinate with the carbonyl group of the ester end thus activates the tertiary — C-Cl bond for homolysis by Ru^{II} (Scheme 3).

Instead of CCl_4, α-halocarbonylcompounds can be employed[31]. Examples are 1,1,1-trichloroacetone, α, α-dichloroacetophenone and ethyl-2-bromoisobutyrate. Aluminum isopropoxide was found



Scheme 3 — Mechanism of methyl methacrylate polymerization initiated by Ru^{II}

to be the best Lewis acid. Polymerization of MMA was conducted at 80°C in toluene using $[MMA]_o$ = 2.0 *M*, [α-halocarbonyl compound]$_o$ = 20 m*M*, $[RuCl_2(PPh_3)_3]_o$ = 10 m*M*, $[Al(OiPr)_3]_o$ = 40 m*M*. The time to reach 50% conversion was about 9 h for ethyl 2- bromo- isobutyrate, 14 h for α, α- dichloroacetophenone and 16 h for 1,1,1-trichloroacetone. The polymerization showed familiar features of a living polymerization, namely constant concentration of growing species with time, $\overline{M}w/\overline{M}n < 1.2$, linear increase of $\overline{M}n$ with time and resumption of polymerization by addition of fresh monomer, resulting in increase in $\overline{M}n$, in direct proportion to monomer conversion and in good agreement with the calculated values. Furthermore, when using the α, α-dichloroacetophenone as initiator, quantitative incorporation of phenyl group into the polymer was demonstrated. The number average end functionality of the initiator moiety (phenyl group) was 1.01, indicating that an α-halocarbonyl compounds in fact serve as an initiator that forms one living poly(MMA) chain per molecule. Results with Ru^{II} catalyzed MMA polymerization are summarized in Table 2.

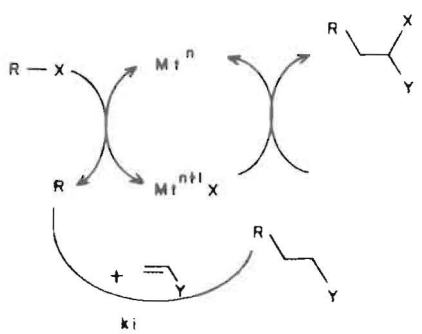
The above reaction, thus involves the reversible activation of a C-Cl bond, at the growing end of the reaction. It thus bears a striking mechanistic resemblance to the living cationic polymerization of isobutylvinyl ether with $HCl/ZnCl_2$ and isobutylene/styrene with cumyl chloride/BCl_3 or $TiCl_4$ systems.

Cobaloximes and Co-porphyrins react reversibly with primary and secondary alkyl radicals. Thus, they are useful initiators for the polymerization of acrylates. Harwood and coworkers[32] have shown that a bisoxime complex of Co^{III} photopolymerizes ethyl acrylate in chloroform at 25°C. 100% conversion could be obtained in 5 h. Various diagnostic tests were performed to show the living character of the chain end. These are: the absence of Tromsdorff effect, linear relationship between $\overline{M}n$ vs conversion and ability to functionalize the chain ends. Although the feasibility of polymerizing both acrylonitrile and vinyl acetate as well as block copolymer synthesis by sequential monomer addition were mentioned, no experimental results were provided. A (tetramethyl porphyrinato) cobalt neopentyl has been shown to initiate the living free radical polymerization of acrylates[33]. Using methyl acrylate[33] (2.5 *M* in benzene)

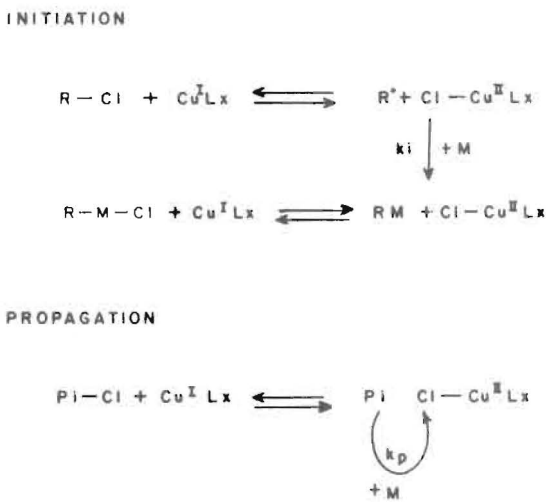
Table 2 — Polymerization of methyl methacrylate using Ru^{II} / halo compounds/Lewis acids

[MMA] *M*	[$RuCl_2(PPh_3)_3$] m*M*	Lewis acid m*M*	Halogen Cpd., m*M*	Temp, °C	Time, h	Conv.%	$\overline{M}n \times 10^{-3}$	$\overline{M}w/\overline{M}n$
2.0[a]	10	40[b]	20[c]	60	4	90	5.2	1.32
2.0[d]	10	40[e]	20[f]	80	60—80	90	10.4	1.15

[a] in *n*-heptane (2.5 mL), [b]Methylaluminiumbis(2,6—di—*tert*—butylphenoxide),[c]CCl_4
[d]in toluene (2.5 mL), [e]Aluminium isopropoxide, [f] α,α,—dichloroacetophenone



Scheme 4 — Atom transfer radical addition reaction



Scheme 5 — Atom transfer radical polymerization reaction

and (TMP) Co-CH_2-$C(CH_3)_2$ (1 x 10^{-3} *M*), at 60°C, resulted in a polymer (70% conversion, $\overline{M}w/\overline{M}n$ = 1.21). The plot of $\overline{M}n$ vs conversion was linear till about 70 to 80% conversion. The living nature of chain end was demonstrated by the synthesis of a methyl acrylate - butyl acrylate copolymer by sequential monomer addition ($\overline{M}n$ (MA-b-BA) 131,400, $\overline{M}w/\overline{M}n$ = 1.29).

Atom Ttransfer Rradical Ppolymerization (ATRP)

Atom transfer radical addition (ATRA) is a well known method for C-C bond formation in organic synthesis[34]. ATRA is also promoted by transition metal catalysts[28]. In these reactions, catalytic amount of transition metal compound act as a carrier of the halogen atom in a redox process (Scheme 4). The high efficiency of metal catalyzed ATRA suggests that the presence of M_{tn}/M_{tn} H redox process provides a low concentration of free radicals resulting in reduced termination reaction between radicals.

The concept of ATRA has been extended to polymerization (atom transfer radical polymerization ATRP) (Scheme 5) of styrene and methyl methacrylate[35]. An alkyl chloride, namely 1-phenyl ethylchloride, is an efficient initiator and a transition metal halide CuCl, complexed with 2,2′-bipyridine, an efficient chlorine atom transfer promoter. For styrene polymerization at 130°C, $\overline{M}n$ increased linearly with conversion. Furthermore, the polymerization was first order in monomer concentration and $\overline{M}w/\overline{M}n$ was in the range of 1.3-1.45. These results suggest a living polymerization process with a negligible amount of irreversible transfer and termination. In the absence of 1- phenylethyl chloride, CuCl or 2,2′-bipyridine, polymers with broad molecular weights distribution and ill- controlled molecular weight were obtained. The method is general and works well with both styrenic and acrylic monomers (Table 3). The end group analysis of poly(methyl acrylate) initiated by 1- phenylethyl chloride by NMR confirms the mechanism (Scheme 5). The polymer has an Ar-CH- CH_3 group at the head and a chlorine atom at the tail.

Table 3 — Atom transfer radical polymerization initiated with RX/CuX/2,2'—bipyridine[a]

Monomer	RX/CuX	Temp., °C	$\overline{M}n$(theory)	$\overline{M}n$ (SEC)	$\overline{M}w/\overline{M}n$
Styrene	1-Phenylethyl chloride/CuCl	130	120, 000	110, 500	1.45
	1-Phenylethyl bromide/CuBr	100	97, 000	93, 300	1.50
	1-Phenylethyl bromide/CuBr	80	8, 300	8, 000	1.25
Methyl acrylate	Ethyl 2-chloropropionate/CuCl	130	30, 500	31, 000	1.40
	Ethyl 2-bromopropionate/CuBr	80	19, 100	21, 500	1.25
	Methyl 2-bromopropionate/CuBr	100	27, 500	29, 100	1.14
Butyl acrylate	Methyl 2-bromopropionate/CuBr	130	15, 000	13, 500	1.50
Methyl[a] methacrylate	Ethyl 2-bromoisobutyrate/CuBr	100	10, 000	9, 800	1.40

[a]Molar ratio of RX/CuX/2,2-bipyridine= 1:1:3, [b] In ethylacetate, 50% by volume

ATRP can also be initiated using conventional radical initiators, e.g. AIBN, instead of 1-phenylethyl halides[36]. In these cases, large excess of $Cu(II)Cl_2$ and 2,2′-bipyridine are required. Typically, polymerization of styrene at 130°C, using ten-fold molar excess of $Cu^{II}Cl_2$ and twenty-fold molar excess of 2,2′-bypyridine results in well controlled polymerization with 95% I_{eff} and $\overline{M}w/\overline{M}n \sim 1.30$. The higher molar excess requirement of $Cu^{II}Cl_2$ was presumably due to its poor solubility in the system. $Cu^{II}Cl_2$ is known to be an efficient and strong inhibitor/retarder of radical polymerization. However, at high temperatures and in the presence of a coordinative ligand such as bipyridine, a reversible activation of the polymeric alkyl chloride occurs.

Under identical conditions, methyl acrylate failed to undergo controlled polymerization. However, use of 2-chloropropionitrile as a coinitiator along with $Cu^{II}Cl_2$ and 2,2′- bipyridine and 1 mol% AIBN relative to 2-chloropropionitrile resulted in controlled polymerization of methyl acrylate.

ATRP can also be initiated by other reactive halides. Recently, Percec and Barboiu[34] have shown that arenesulfonyl chloride in the presence of $Cu^{I}Cl$ and 2,2′-bipyridine initiates the bulk polymerization of styrene[37]. Good molecular weight control was obtained. The polydispersities were in the range of 1.50 - 1.80. Both arylsulfonyl and chlorine groups were detected at the terminal end of the polymer.

One of the disadvantages of the Cu^{I}/Cu^{II} alkyl halide or arenesulfonyl halide systems is that they are heterogeneous. 2,2′-Bipyridine only partially solubilizes the catalyst system. This limits the complete monomer conversions using the above catalysts. It has been found that 4,4′-dinonyl- 2,2′-bipyridine forms a very soluble complex with $Cu^{I}Cl$ and can be used for the homogeneous polymerization[38]. Use of homogeneous catalysts improves the molecular weight distribution (1.30 vs 1.4 for heterogeneous catalysts). Recently, the kinetic features of ATRP of methyl acrylate and styrene have been elucidated[39].

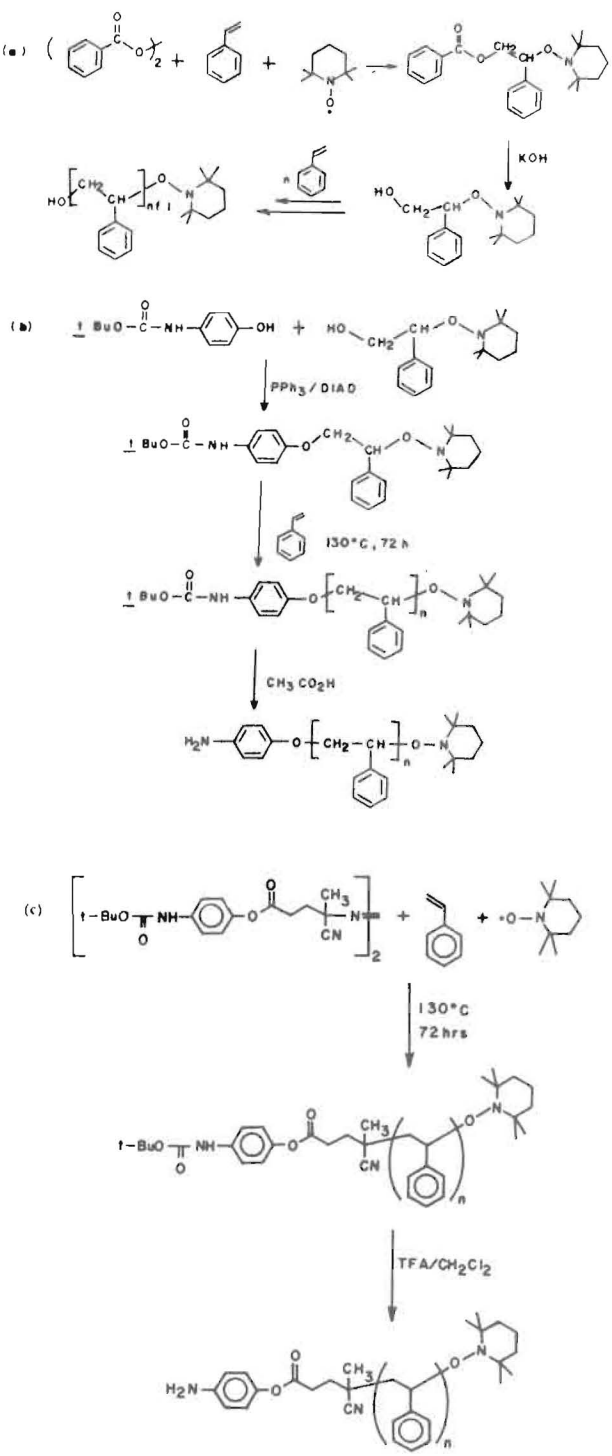
ATRP, thus, is a simple, inexpensive and general method for controlled radical polymerization of styrene and acrylate monomers. The presence of a cata-

lytic amount of growing radicals and fast equilibration between growing radicals and dormant species are essential for successful atom transfer radical polymerization. Under well-defined conditions, ATRP can produce poly(styrene) with $\overline{M}w/\overline{M}n = 1.05$ ($\overline{M}n = 8,777$ and conversion = 78%)[40].

Synthesis of Polymers with Controlled Structures/Architectures Using Living Radical Polymerization

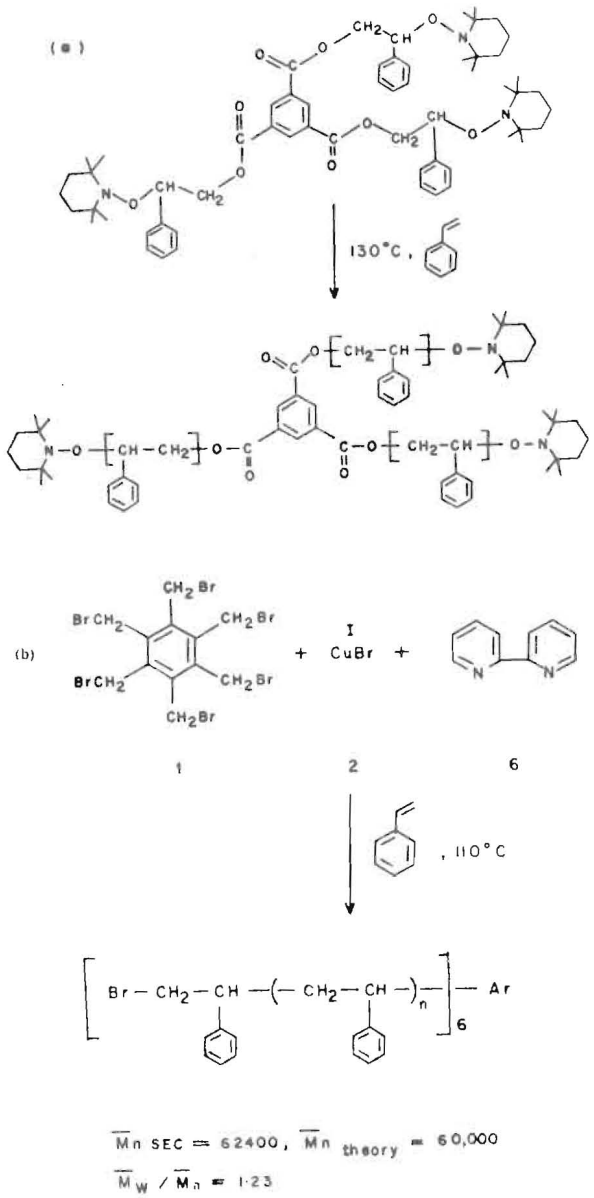
The availability of controlled methods for polymerization opens the doors for new polymer synthesis. It is, therefore, not surprising that availability of efficient methods for controlled radical polymerization has stimulated renewed interest in this area. Novel strategies have been explored for the synthesis of end functionalized polymers[41,42], graft and star polymers [42,43], hyperbranched polymers[44-46], random and block copolymers[47,48]. Using nitroxide mediated stable free radical polymerization block copolymers of poly(styrene) and *t*-butylacrylate and 4-vinylpyridine have been synthesized. Triblock copolymers of poly(styrene) - poly(isoprene) - poly(styrene) were prepared by sequential monomer addition[49].

Functionalized unimolecular initiators derived from monoadducts of benzoyl peroxide, styrene and TEMPO were prepared (Scheme 6). Using these functionalized initiators, hydroxy and amino end functionalized poly(styrene)s were prepared[41]. Possibilities of synthesizing functionalized polymers using ATRP have been pointed out[42]. Use of initiators such as Y-R-X, where Y = -CO_2H, -OH, -CN, C=C, naphthyl and X = Cl, Br, should yield polymers with end functionalization Y. Block copolymers of methyl acrylate with styrene by ATRP has been reported[42]. Polymerization of methyl acrylate by 1-phenylethyl chloride/Cu^I Cl/bipyridyl at 130°, resulted in a poly(methyl acrylate) with a terminal chlorine end group. Addition of styrene and further polymerization resulted in a block copolymer, poly[(methyl acrylate)-b-styrene]. The $\overline{M}n$ of polymethyl acrylate) block was 2080 ($\overline{M}w/\overline{M}n = 1.25$), whereas that of the poly(styrene) block was 6240 ($\overline{M}w/\overline{M}n = 1.35$). ATRP has been applied to homopolymerization of acrylonitrile and its block copolymerization with *n*-butylacrylate and 2-ethylhexylacrylate[50].



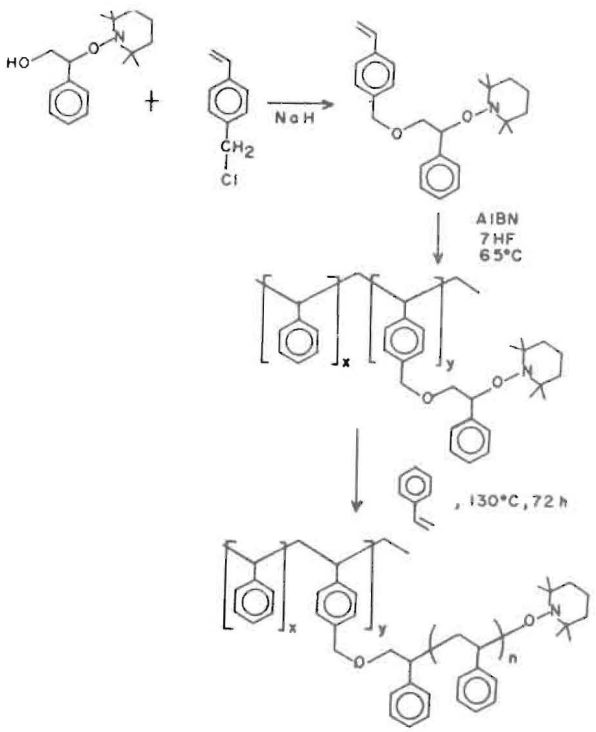
Scheme 6 — End functionalized polymers by stable free radical mediated polymerization

Star shaped polymers have been successfully synthesized using both stable free radicals mediated and atom transfer radical polymerizations (Scheme 7).



Scheme 7 — Branched polymers using living free radical polymerizations

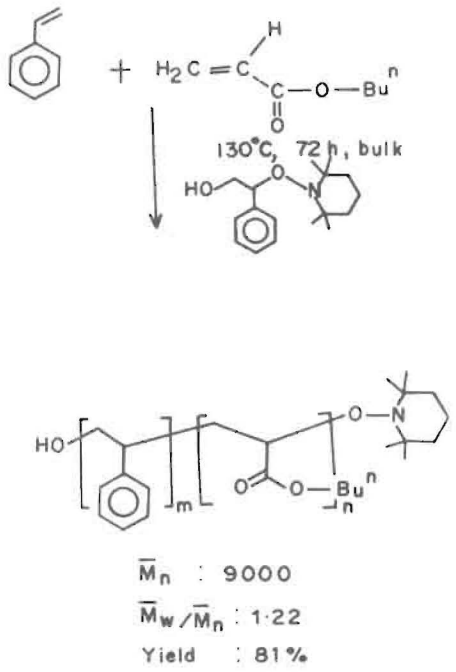
Three-arm poly(styrene)s and six arm poly(styrene)s, poly(methyl acrylate)s and poly(methyl methacrylate)s have been synthesized[42,43]. Three arm poly(styrene)s with arm molecular weights $\overline{M}n$ (SEC) = 22,000, $\overline{M}n$ (theory) = 24,000 and $\overline{M}w/\overline{M}n$ = 1.09 were prepared in 88% yield. The interesting feature of the six=arm polymers prepared by ATRP is that every arm contains a halogen terminal group, capable of being further functionalized (Scheme 7b).



Scheme 8 — Graft copolymerization of styrene using living free radical polymerization

Graft copolymers have also been prepared using living free radical polymerization techniques (Scheme 8). Random copolymers of styrene with methyl methacrylate or *n*-butyl acrylate have been synthesized (Scheme 9). Traditional methods such as anionic, cationic or group transfer polymerization techniques are not suitable for the synthesis of random copolymers from disparate vinyl monomers such as styrene and acrylates. Polymers with a range of composition, controlled molecular weight and end functionality and narrow polydispersities (1.1 - 1.6) have been reported.

Recently, Frechet and coworkers[44] have proposed a new class of vinyl polymerization, namely, self-condensing vinyl polymerization, which promises to be a simple method for the synthesis of complexed branched polymer structures (Scheme 10). This principle has been applied to controlled and living radical polymerization of suitable[45,46] precursor monomers (Scheme 11) to yield hyperbranched polystyrenes[45,46].

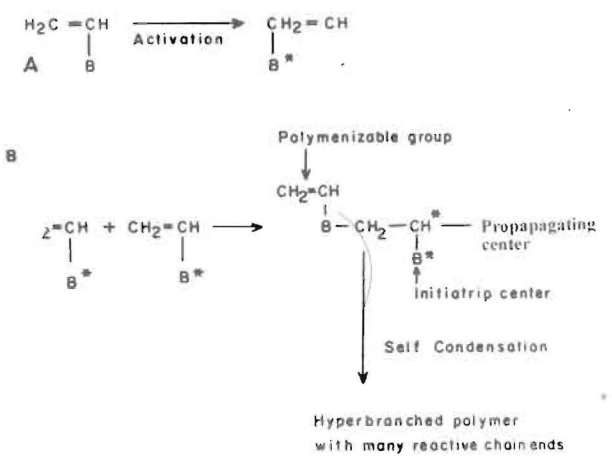


Scheme 9 — Random copolymerization of styrene and butyl acrylate using living free radical polymerization

(Scheme 11) to yield hyperbranched polystyrenes[45,46].

Concluding Remarks

The emergence of the living radical polymerization chemistry capable of producing polymers with controlled molecular weights and narrow molecular weight distributions within the last three years has opened up new horizons in polymer synthesis. In a very short duration, chemists have exploited this technique, creatively, for the synthesis of polymers with well defined architectures and novel functional polymers, previously obtainable only under synthetically more rigorous living anionic or cationic polymerization conditions. More significantly, the emergence of this chemistry, has further unified the mechanistic concepts underlying many of the well known living polymerization processes, namely anionic polymerization of methyl methacrylate, cationic polymerization of styrene, isobutylene and isobutyl vinyl ether and group transfer polymerization of methyl methacrylate[51]. In every case, enhanced livingness with negligible contributions from chain breaking or termination reactions has been achieved by invoking the concept of "reversible termination" involving an "active" species in rapid equilibrium with a dormant species.



Scheme 10 — Self-condensing vinyl polymerization

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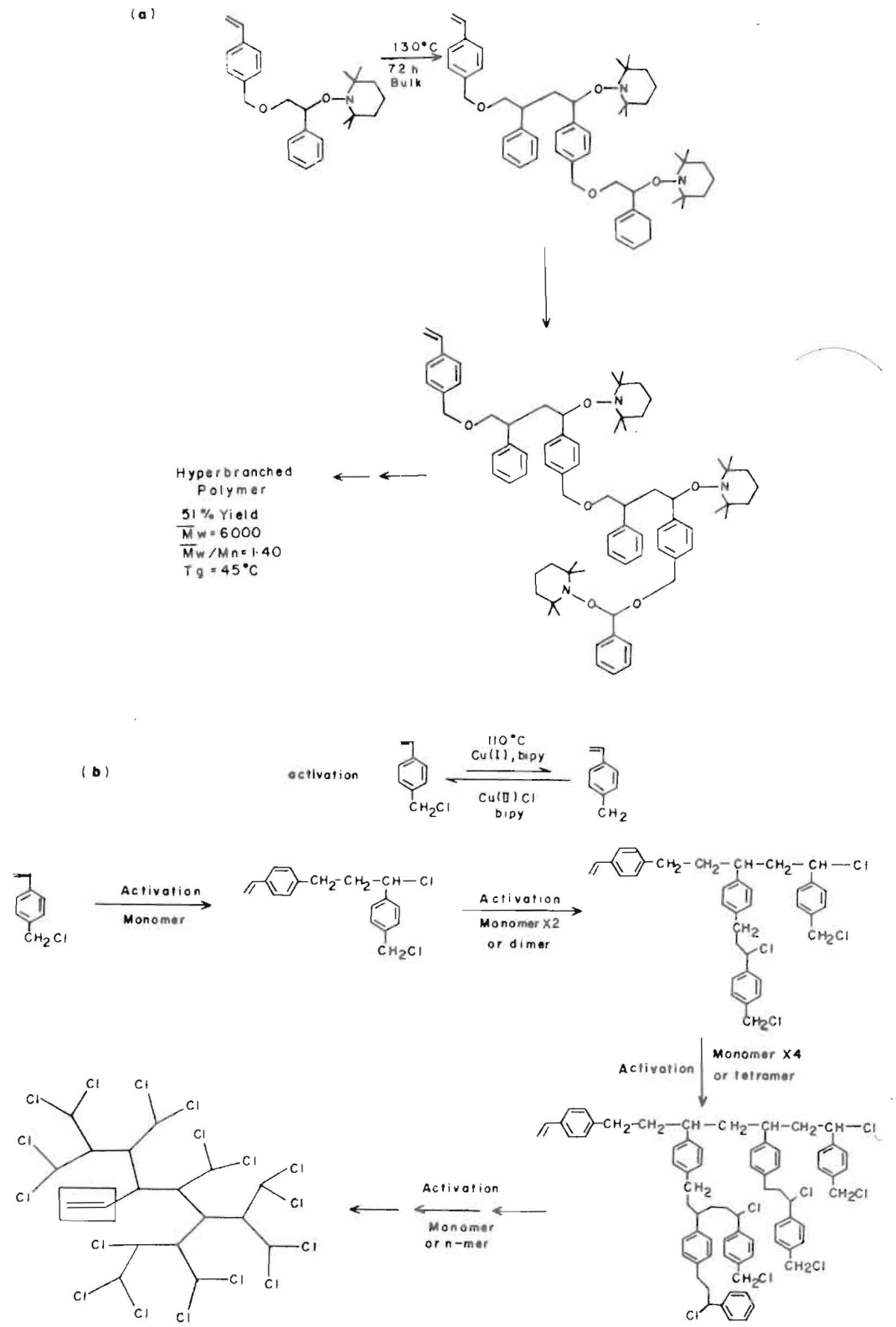
Abbreviations

AIBN =Azo-bis-isobutyronitrite; BPO =Benzoyl peroxide; $[C^*]$ =Concentration of active species; DPn =Number average degree of polymerization; I_{eff} =Initiator efficiency, defined as the ratio of $\overline{M}n$, as determined by SEC to $\overline{M}n$, calculated from $[M]_o$ and $[I]_o$; $[I_o]$. =Initial initiator concentrations; K_p =Rate constant of propagation; K_t =Rate constant for termination; $\overline{M}n$ =Number average molecular weight; $[M]_o$ =Initial initiator concentration; $\overline{M}w$ =Weight average molecular weight; $\overline{M}w/\overline{M}n$ =Polydispersity index, ratio of weight average to number average molecular weights; R_p =Overall rate of polymerization; SEC = Size exclusion chromatography; TEMPO =2,2,6,6-tetramethyl-1-piperidinyloxy.



Scheme 11 — Living free radical self-condensing vinyl polymerization approach to hyper-branched poly (styrene)s

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