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MACROTHIOLS THROUGH FREE RADICAL CHAIN TRANSFER: SYNTHESIS, KINETICS, AND APPLICATION IN BLOCK COPOLYMER SYNTHESIS

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Key Words: Free Radical Chain Transfer, Macro Chain Transfer Agent, Macrothiol, Diblock Copolymer

ABSTRACT

Macro chain transfer agents based on mercaptan terminated-polymethyl methacrylate (macrothiol, PMMA-SH) were obtained by low-conversion free radical polymerization of methyl methacrylate in presence of 1,6-hexane dithiol as chain transfer agent. The chain transfer constant of 0.82 ensured good functionality and relatively narrow dispersity for the formed macrothiol. On increasing the conversion, the molecular weight of the macrothiol increased and its functionality decreased. A kinetic model was proposed which could satisfactorily explain these variations. Free radical polymerization of styrene in presence of PMMA-SH as chain transfer agent furnished the PS-PMMA diblock copolymer. Styrene exhibited a transfer constant (Ctr) of 3.37 for the macrothiol which was practically the same as that for 1,6-hexane dithiol for the same monomer. The length of polystyrene block in the copolymer decreased with increase in concentration of the macrothiol in the reaction medium. However, the block length was more than that theoretic-

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cally expected which was attributable to the effect of diffusion controlled kinetics. The block copolymers were characterized by elemental analysis and by gel permeation chromatography using multiple detectors. Attempts to synthesize macrothiol of butyl acrylate and styrene and corresponding block copolymers were not successful due to secondary reaction during chain transfer in these cases.

INTRODUCTION

Block copolymers are required extensively in various fields such as emulsifiers, thermoplastic elastomers, polymer blend compatibilizers, adhesives, etc. [1, 2]. Several free radical techniques have been known for their synthesis. While most of the techniques are based on the initiation of monomer using polymeric initiators [3-5], a few techniques represent the use of polymeric chain transfer agents [6-8]. Thus, poly phenyl sulfides [6] and poly thiuram disulfides [7, 8] have been used to derive multi-block copolymers. Except for thiuram disulfides, other polymeric transfer agents have relatively low chain transfer constant and, consequently, the yield of block copolymer in such cases is not good. Mercaptans have excellent chain transfer properties. Hence, polymers bearing these groups could be excellent precursors for deriving block and graft copolymers. In this way, Gregor *et al.* [9] have reported the use of pendant mercaptan-bearing polymers in deriving graft copolymers. The SH-groups were generated through a sequence of reactions involving chemical protection and deprotection of SH- groups in monomer and in polymer. Similarly, SH-bearing polysiloxanes have been used as polymeric chain transfer agents to graft vinyl segments onto it [10].

In this paper, we report a single-step free radical route to derive SH-terminated vinyl polymer and its use as macro chain transfer agent in free radical polymerization of another monomer to result in diblock copolymer. The kinetics of the formation of macrothiol has been described in detail.

EXPERIMENTAL

Materials

Hexane dithiol (HDT) was procured from Aldrich, USA and was used as such. Methyl methacrylate (MMA, CDH, India) and styrene (Alfa Biochem),



both free of polymer, were purified by passing through a basic alumina column. Azobisisobutyronitrile (AIBN) and benzoyl peroxide were recrystallized from methanol and chloroform, respectively.

Instruments

Gel Permeation Chromatography (GPC) was performed using a Waters GPC model 3000 equipped with a LC 481 UV detector and a differential refractive index R 401 (RI) detector. Polystyrene standards were used for calibration and tetrahydrofuran as eluent. FTIR was recorded on a Nicolet 510P instrument. Elemental analyses were performed on a Perkin Elmer Elemental Analyzer, model-2400.

Determination of Ctr and Synthesis of Macrothiol

Calculated amounts of MMA (or styrene), 1,6-hexanedithiol and AIBN were mixed together in a pyrex glass tube, and sealed in vacuum after freezing, evacuating, and thawing. The content was heated in a thermostated water bath. After the polymerization, the reaction mixture was diluted with tetrahydrofuran and precipitated into 30-fold volume of n-hexane. The precipitated polymer was isolated by filtration. It was purified by dissolution in THF and reprecipitation into hexane twice, consequently, any contamination in the polymer by HDT could be eliminated. The filtrate on evaporation did not leave any dissolved polymer. The isolated polymer was dried in vacuum at 50°C and weighed. For determination of transfer constant, conversion was limited to less than 10%. The polymer was characterized by GPC analysis and the mercaptan-content was estimated by chemical analysis using iodimetry.

Determination of Transfer Constants for Macrothiol

The macrothiol and styrene were taken in different proportions at fixed concentration (weight percentage) of AIBN, and were polymerized in sealed evacuated tubes. The contents after dilution with THF were dropped into 30-fold volume of methanol: acetone (3:1) mixture to isolate the polymer. It was purified by dissolution in THF and by reprecipitation in to the same solvent mixture. The unreacted macrothiol solubilized in the precipitant which was ensured from the GPC analysis of the precipitated polymer. The filtered polymer was dried, weighed, and its molecular weight was estimated by GPC.

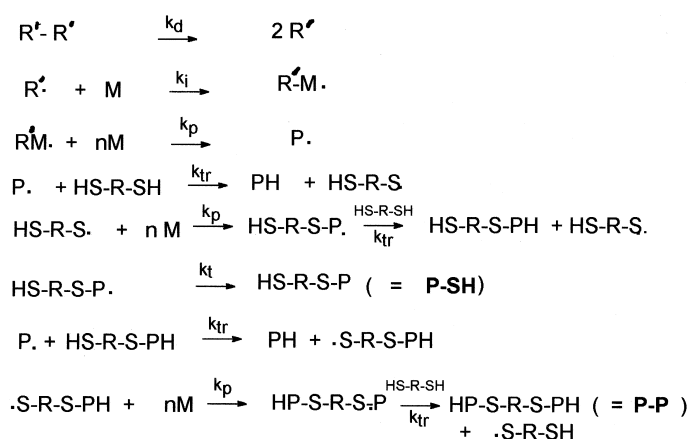


Synthesis of Macrothiol at Different Conversion

MMA, HDT and AIBN were charged into a two-necked round bottomed flask under N_2 atmosphere. The contents were heated under magnetic agitation in a magnetic stirrer vacuum thermostated oil bath (IKA, Germany). Samples were withdrawn at different time intervals, weighed, diluted with THF, and precipitated into hexane. The precipitated polymer was dissolved in THF and reprecipitated into hexane. It was filtered, dried under vacuum at 50°C , and weighed. Conversion was estimated gravimetrically. Molecular weight was determined by GPC and SH-content by chemical analysis (details in Table 3).

Synthesis and Purification of Polystyrene-PMMA Diblock Copolymer

The PMMA-macrothiol, styrene and benzoyl peroxide were weighed into glass tubes or round bottomed flask. They were sealed in vacuum as usual. Polymerization was done at 85°C in a water bath. After the polymerization, the contents were diluted with THF and were added dropwise to 30-fold volume of methanol containing 20 volume percentage of acetone. The precipitated polymer was dissolved in THF and reprecipitated in the same way. Methanol-acetone mixture removed the unreacted macrothiol present in the copolymer as ensured from trial precipitation using the same macrothiol. GPC of the precipitated polymer also ensured absence of any macrothiol contaminant. The homopolystyrene if any, in the above precipitated polymer was removed by dissolving it in THF and precipitation into a large excess of cyclohexane for



Scheme 1. Mechanism of polymerization of MMA in presence of hexane dithiol.



comparatively high macrothiol loading (in the original feed) and hexane-cyclohexane mixture for low macrothiol-content. This was done twice. The filtrate contained small amounts of polystyrene and was practically devoid of any copolymer as evidenced from the IR spectrum of the residue in the filtrate which did not exhibit any characteristic absorption of the carbonyl group of PMMA. The polymer was filtered, dried and weighed. Characterization was done by elemental analysis and by GPC. The composition was obtained from the carbon-content and the homogeneity of the polymer was confirmed by GPC analysis using RI & UV detectors.

RESULTS AND DISCUSSION

Determination of Ctr

A macro chain transfer agent (macrothiol) was obtained when MMA was polymerized in the presence of 1,6-hexanedithiol as shown in Scheme 1. At lower conversion, and in the presence of appreciable concentration of the dithiol in the medium, the probability for transfer to the terminal SH-group in the initially formed polymer is minimal. Consequently, the reaction leads to formation of mercaptan-terminated polymer. In such a case, the mercaptan-functionality of the polymer depends principally on the transfer constant, Ctr of the dithiol for the given monomer. Ctr was determined by the classical method of Mayo using the equation:

$$\frac{1}{DP} = \frac{1}{DP_0} + \frac{Ctr[SH]}{[M]}$$

where, DP is the degree of polymerization when the concentration of the mercaptan groups in the chain transfer agent is [SH] and that of the monomer is [M]. DP₀ is the degree of polymerization in the absence of any chain transfer agent. The reaction conditions for determination of Ctr for MMA and styrene are given in Table 1. This calculation is based on the assumption that the participation of the mercaptan groups on the initially formed macrothiol in subsequent transfer reaction does not add significantly to the molecular weight of the polymer. This has been confirmed in a separate set of experiments where, the molecular weight of the polymer was monitored as a function of conversion, and, in which case the molecular weight was found to be fairly constant till about 40% conversion (see later). The kinetic plot for



TABLE 1. Determination of Ctr of HDT for Styrene and MMA at 70°C.

System	[HDT], mol/Lx10 ²	Conversion (%)	Mn	Mw/Mn	Ctr	
					Apparent	Effective
Styrene	2.22	7.4	2840	2.48	6.74 ± 0.83	3.37 ± 0.42
	4.44	8.5	1610	2.40		
	6.66	12.5	1080	2.46		
	8.88	10.0	860	2.03		
	10.1	4.6	550	1.66		
MMA	1.33	4.5	19300	2.30	0.820± 0.016	
	2.00	4.9	10980	2.45		
	4.00	5.9	6410	2.30		
	6.00	9.7	4440	2.11		
	8.00	7.2	3360	2.04		
	10.66	8.2	2550	1.77		

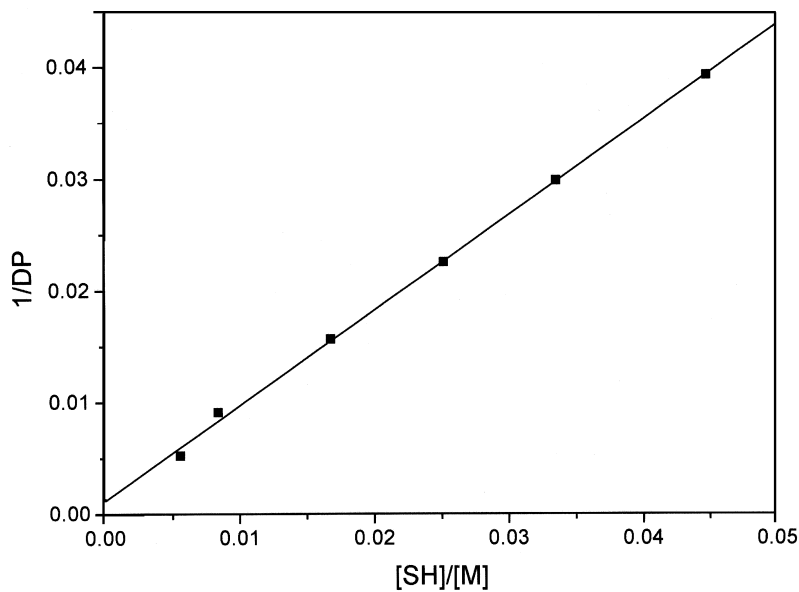


Figure 1. Mayo's plot for determination of Ctr for MMA.

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determination of Ctr for MMA is shown in Figure 1. The Ctr for MMA was obtained as 0.82, and for styrene, 3.37 (discussed later). The high Ctr values guarantee good functionality for the formed macrothiols.

Synthesis of Macrothiols

In this study, macrothiols required for subsequent application in block copolymer synthesis were prepared by polymerization of MMA in the presence of hexane dithiol and by limiting the monomer conversion to less than 30%. The molecular weights were varied using a different concentration of hexanedithiol. Their functionalities were determined by chemical analysis of the mercaptan group and from the molecular weight determined by GPC. The results are given in Table 2. Functionality shows a broad range and it is strongly dependent on conversion, and that good functionality is obtained only on limiting the conversion to less than 10%. The functionality was found to decrease as conversion increased, implying participation of the initially formed macrothiol in subsequent chain transfer reaction. As a result of this, the molecular weights of the polymer was more than the theoretical ones based on the assumption that the mercaptan is monofunctional. The nonfunctional part in the macrothiol could be PMMA molecule formed by transfer to both the SH-groups of HDT. The nonfunctional polymer normally does not interfere in the block copolymer synthesis and can be removed from the final block copolymer by a suitable solvent extraction method. The molecular weight of the effective chains (capable of transfer) are calculable by the Mayo's equation and has been included in the table.

TABLE 2. Synthesis Conditions and Characteristics of Macrothiols, Polymerization Temperature 70°C

System	[HDT], mol/Lx10 ²	Conversion (%)	Mn	Mw/Mn	Ctr	
					Apparent	Effective
Styrene	2.22	7.4	2840	2.48	6.74 ± 0.83	3.37 ± 0.42
	4.44	8.5	1610	2.40		
	6.66	12.5	1080	2.46		
	8.88	10.0	860	2.03		
	10.1	4.6	550	1.66		
MMA	1.33	4.5	19300	2.30	0.820± 0.016	
	2.00	4.9	10980	2.45		
	4.00	5.9	6410	2.30		
	6.00	9.7	4440	2.11		
	8.00	7.2	3360	2.04		
	10.66	8.2	2550	1.77		



Dependency of Molecular Weight and Functionality of Macrothiol on Conversion; Kinetic Analysis

The various reactions taking place during free radical polymerization of MMA in the presence of HDT are shown in Scheme 1.

The SH-groups are formed at chain terminals by way of chain transfer to the dithiol to result in the macrothiol. The functionality (F_n) of the formed macrothiol should depend, *a priori*, on the chain transfer constant (C_{tr}) of the dithiol (HDT) and is given by [11]

$$F_n = C_{tr} \cdot DP \cdot [SH]/[M] \quad (1)$$

where, $C_{tr} = k_{tr}/k_p$, $[SH]$ is the concentration of mercaptan groups and $[M]$ that of the monomer at any given instant when, DP is the degree of polymerization.

It is possible that the initially formed macrothiol participate in the transfer reaction that could alter the molecular weight and the functionality of the polymer as polymerization advances. This can be analyzed from the kinetic model as follows.

Case 1, Monofunctional Chain Transfer Agents

In the case of a monofunctional chain transfer agent like alkyl monomercaptan ($R-SH$), the kinetics is governed by the conventional transfer reaction. The relative rate of change of thiol and monomer at any given instant is given as,

$$d[SH]/d[M] = C_{tr} [SH]/[M] \quad (2)$$

where $[SH]$ is the concentration of thiol (in terms of molar concentration of SH groups) and $[M]$, that of the monomer.

If α is the conversion with respect to the monomer (i.e. extent of polymerization), then $[M] = [M]_0 (1-\alpha)$, where, $[M]_0$ is the initial concentration of the monomer.

Integration of Equation 2 over the conversion range from 0 to α gives,

$$[SH] = [SH]_0 (1-\alpha)^{C_{tr}} \quad (3)$$

where, $[SH]_0$ is the initial concentration of transfer agent.

The degree of polymerization of the instantaneously formed polymer at conversion α (i.e. DP_{inst}) is given as

$$1/DP_{inst} = 1/DP_0 + C_{tr} [SH]/[M] = 1/DP_0 + C_{tr} [SH]_0/[M]_0 (1-\alpha)^{(C_{tr}-1)} \quad (4)$$



DP_0 is the degree of polymerization in the absence of the chain transfer agent. When C_{tr} is fairly high as in the present case, the term $1/DP_0$ is negligible in comparison to $1/DP_{inst}$ and the variation in the former as a result of change in concentrations of the initiator and monomer during the course of polymerization has practically no effect in deciding the instantaneous molecular weight (in fact, the molecular weight is represented to the best approximation by the second term on the right hand side of Equation 4. Therefore, for all practical purposes, DP_0 can be considered as invariant without committing any serious error.

If $d\alpha$ is the change in conversion at conversion α , the number of chains produced instantaneously (N_{inst}) is proportional to $d\alpha/DP_{inst}$, where DP_{inst} is the degree of polymerization of the instantaneously produced polymer chains at this conversion,

$$\text{i.e. } N_{inst} = k \cdot d\alpha/DP_{inst}, \text{ } k \text{ is a proportionality constant}$$

The cumulative number average DP (i.e. DP_c), at conversion α can be obtained by summing up the number of all such chains.

$$DP_c = \frac{k \int_0^\alpha (d\alpha/DP_{inst}) \cdot DP_{inst}}{k \int_0^\alpha (d\alpha/DP_{inst})} = \frac{\alpha}{\alpha/DP_0 - [SH]_0/[M]_0 \{ (1-\alpha)^{C_{tr}} - 1 \}} \quad (5)$$

The cumulative number average functionality (F_{nc}) of the polymer at conversion α is given as,

$$F_{nc} = \frac{\int_0^\alpha F_{n_{inst}} \cdot k \cdot d\alpha/DP_{inst}}{\int_0^\alpha k \cdot d\alpha/DP_{inst}} \quad (6)$$

where, $F_{n_{inst}}$ is the functionality of the instantaneously formed polymer, given as

$$F_{n_{inst}} = DP_{inst} C_{tr} [SH]/[M] \quad (7)$$

Substituting this in Equation 6 and integrating,

$$F_{nc} = \frac{- [SH]_0/[M]_0 \{ (1-\alpha)^{C_{tr}} - 1 \}}{(\alpha/DP_0) - [SH]_0/[M]_0 \{ (1-\alpha)^{C_{tr}} - 1 \}} \quad (8)$$

The variations in DP_c and F_{nc} for a hypothetical case of polymerization of MMA using a monofunctional chain transfer agent of the type R-SH of $C_{tr} = 0.82$ and at $[SH]_0/[M]_0 = 0.56$ is shown in Figure 2. Whereas the molecular weight decreases with conversion, F_{nc} is more or less constant and is quite inde-

pendent of it. Here, F_{n_c} refers to the functionality of the polymer with respect to the sulphur-born group.

Case (ii), Difunctional Chain Transfer Agent

In this case, the initially formed macrothiol also participates in subsequent transfer process (Scheme 1) which will alter the molecular weight and functionality of the resultant polymers as the reaction advances.

The degree of polymerization of the instantaneously formed polymer at conversion α is given as,

$$1/DP_{inst} = 1/DP_0 + Ctr [SH]/[M] + Ctr'[PSH]/[M] \tag{9}$$

Where, $[SH]$ and $[PSH]$ are the concentrations of the mercaptan functions of the dithiol and macrothiol, respectively at conversion α and whose chain transfer constants are Ctr and Ctr' respectively. DP_0 is the DP in the absence of any of these chain transfer agents, the variations in which may not have significant effect on DP_{inst} as discussed early and may be considered as invariant.

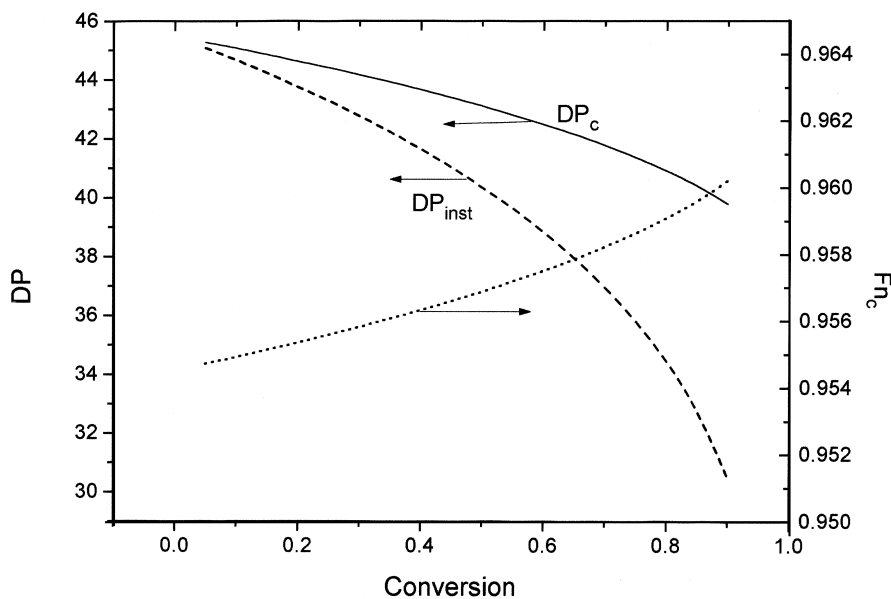


Figure 2. Theoretical dependencies of DP and F_{n_c} on conversion for polymerization of MMA using monofunctional chain transfer agent of $Ctr = 0.82$, --- DP_{inst} , — DP_c , F_{n_c} .

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The net concentration of PSH can be obtained from the relationship between the relative changes in concentration of the dithiol (HDT in this case) and the macrothiol (PSH) with respect to the monomer, given by the differential expression (10),

$$-d[\text{PSH}]/d[M] = d[\text{HDT}]/d[M] - \text{Ctr}' [\text{PSH}]/[M] \quad (10)$$

For shorter polymer chains, $\text{Ctr} = \text{Ctr}'$ as has been proven in the case of styrene in this study (see later).

$d[\text{HDT}]/d[M] = 2 \times \text{Ctr} [\text{HDT}]/[M]$, the factor 2 intervening due to the difunctional nature of HDT. Substituting for $[M] = [M]_0(1 - \alpha)$, and $[\text{HDT}] = [\text{HDT}]_0(1 - \alpha)^{2\text{Ctr}}$ in Equation 10, and integrating it over the conversion range up to α ,

$$-[\text{PSH}] = \{[\text{HDT}]_0 \cdot \{(1 - \alpha)^{2\text{Ctr}} - 1\}\} - \int_0^\alpha \text{Ctr} \cdot [\text{PSH}] d[\ln(1 - \alpha)] \quad (11)$$

For extremely small increments of α , the changes in $[\text{PSH}]$ may be considered to be insignificant, rendering $[\text{PSH}]$ practically constant during this interval, thereby permitting the integration of the above differential Equation 11

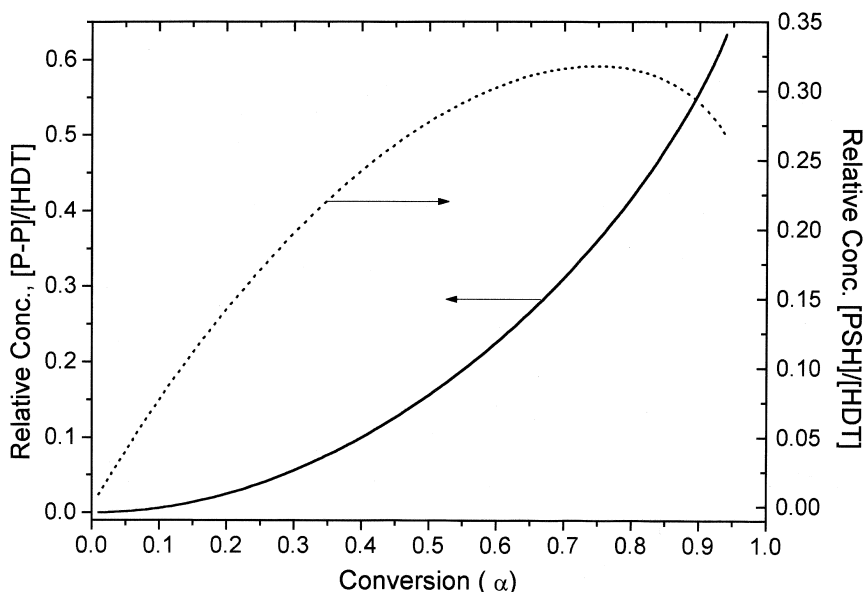


Figure 3. Variations in concentrations of PSH and — P-P with conversion for polymerization of MMA in the presence of HDT with $[\text{HDT}] = 0.133 \text{ mol/L}$.



numerically for a given concentration of $[HDT]_0$ to find $[PSH]$ at any given conversion, α . $[PSH]$ has thus been calculated using the above equation with the help of a *BASIC* computer program at $[HDT] = 0.133$ mol/L and its variation with conversion is shown in Figure 3. It may be noted that at higher conversion, PSH tends to decrease with conversion.

As a result of transfer to PSH, the molecular weight of the polymer formed, i.e. P-P is twice that of PSH (Scheme 1).

The cumulative number average degree of polymerization at conversion, α can be found from the concentrations of PSH and that of P-P and from their respective molecular weights.

Concentration of P-P is given as

$$[P-P] = \int_0^\alpha \text{Ctr.}[PSH]d[\ln(1-\alpha)], \quad (12)$$

which can be obtained during numerical integration of Equation (11).

The relative variations in concentrations of both PSH and P-P, calculated in a typical case of polymerization of MMA in presence of HDT at a concentration of 0.133 mol/L, is shown in Figure 3. $[P-P]$ is seen to increase continuously. The average degree of polymerization is obtained from the relationship,

$$DP_c = \{[PSH] \cdot DP_{PSH}\} + \{[P-P] \cdot 2 \cdot DP_{PSH}\} / \{[PSH] + [P-P]\} \quad (13)$$

DP_{PSH} is given by Equation 5.

In this case, the cumulative functionality of the polymer at conversion α can be obtained from the relation,

$$Fn_c = \{[PSH] \cdot Fn_{PSH}\} / \{[PSH] + [P-P]\} \quad (14)$$

Fn_{PSH} is obtainable from Equation 1. Variations in DP_c and Fn_c can be found in Figure 4 for a typical case of polymerization of MMA with HDT at a concentration of 0.133 mol/L. DP increases and Fn decreases systematically with conversion.

The end-functionalization of PMMA by SH-group was indirectly confirmed from a near doubling of the molecular weight of the macrothiol (obtained at low conversion) when it was oxidized by I_2 which couples the polymer chains in pairs.



The dependency of the molecular weight and functionality on conversion was experimentally examined by polymerizing MMA in bulk and by



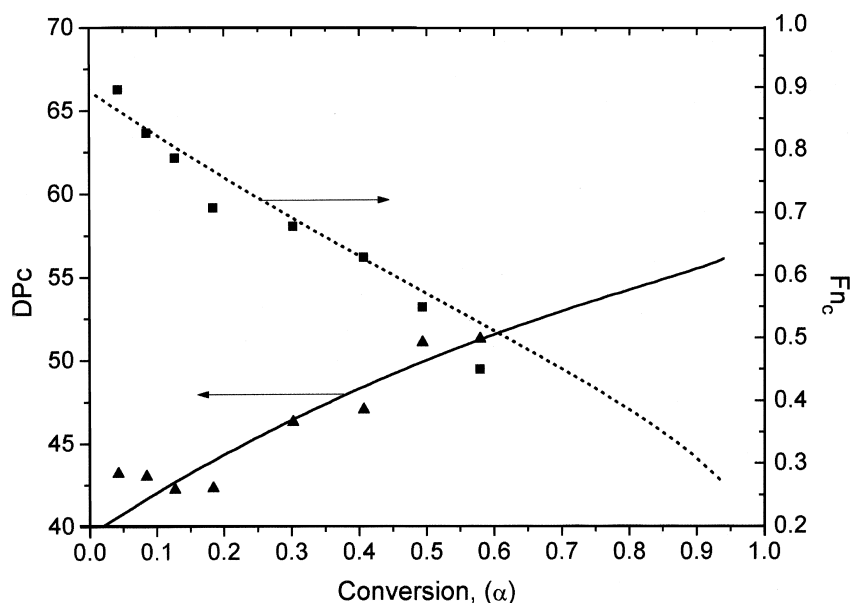


Figure 4. Cumulative molecular weight (DPC) and functionality (F_{n_c}) of macrothiol formed in presence of HDT (0.133 mol/L), \cdots theoretical F_{n_c} , \blacksquare - experimental F_{n_c} , — theoretical DPC, \blacktriangle - experimental DPC.

analyzing the molecular weight and functionality of the polymer at different conversion. Typical results given in Table 3, show that the molecular weight increases with conversion. Since the transfer constant is less than unity, the molecular weight would be expected to decline with conversion in case the transfer agent were monofunctional as depicted in Figure 2. The increase in molecular weight with conversion in this case, therefore, confirms chain growth from the terminal of the initially formed macrothiol as the reaction advances in conformation with the kinetic model proposed. This also results in a decline in functionality.

The experimental variations in DPC and F_{n_c} with conversion is also shown in Figure 4. A fairly good tally within experimental limits can be found between the theoretical and experimental values of both DPC and F_{n_c} and their variations with conversion. In this experiment, the maximum conversion was limited to about 65% since beyond this, the system tends to gel and the kinetics deviate from the chemically controlled one. This is evidenced from the plot of $\ln(1-\alpha)$ against *time* for this experiment shown in Figure 5, where good linearity



TABLE 3. Synthesis of Macrothiols of MMA at Varying Conversion, $[HDT] = 0.133 \text{ mol/L}$, $AIBN = 6.93 \times 10^{-3} \text{ mol/L}$, Temperature 70°C

Time of polymn. (min)	Conversion (%)	Mn	Mw/Mn	SH%	Fn
20	4.25	4300	2.06	0.69	0.90
35	8.50	4325	2.15	0.63	0.83
50	12.70	4220	2.22	0.62	0.79
74	18.40	4230	2.26	0.55	0.71
120	30.20	4630	2.32	0.48	0.68
160	40.75	4670	2.35	0.45	0.63
195	49.35	4820	2.26	0.34	0.50
225	57.85	5120	2.18	0.28	0.44

is observed for conversion up to about 50%. The study implies that it is imperative to limit the conversion to get good functionality.

Synthesis and Characterization of Diblock Copolymer

The macrothiols (PMMA-SH) were used as macro chain transfer agents for polymerization of styrene to derive the PMMA-*b*-PS copolymer as per Scheme 2.

The efficiency of the method depends on the chain transfer capability of the macrothiol which was determined for a typical case of PMMA-SH with styrene, whose details are compiled in Table 4. The corresponding plot for determination of Ctr can be found in Figure 6. While calculating the DP of the polymer for the Mayo's plot, the effective molecular weight of the polymer was corrected after accounting for the segment contributed by the PMMA sequence incorporated in it as a result of transfer to PMMA-SH. The transfer constant was calculated as 3.26 as against the effective value of 3.37 for hexane dithiol/styrene pair (Table 1 and Figure 6). This implies that the transfer property of the mercaptan group is practically unaffected by its location on PMMA. This may be because the macrothiol studied here is of relatively low molecular weight and that the limited conversion does not lead to any diffusion control for the kinetics that would have arisen in a viscous medium. In other words, the trend could be different when it concerns higher molecular weight macrothiols and high conversion, high viscous polymerization systems. The high chain



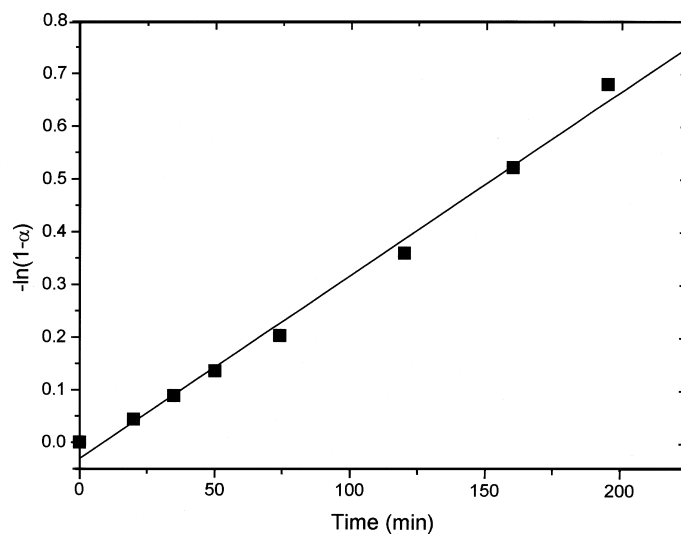
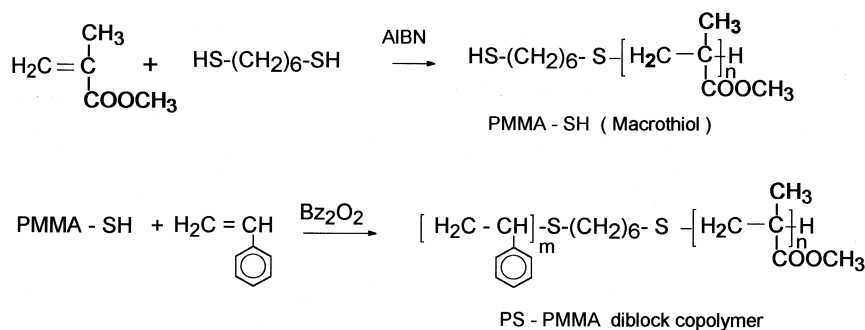


Figure 5. Time-conversion relationship for the polymerization of MMA in presence of HDT, [HDT] = 0.133 mol/L, 70 °C.

transfer constant of PMMA-SH for styrene ensures better formation of block copolymer.

In such a synthesis, the PMMA block length can be regulated by the choice of the macrothiol of desired molecular weight. The length of polystyryl block is dictated by the chain transfer constant of the macrothiol and its concentration in the reaction medium.



Scheme 2. Formation of macrothiol and diblock copolymer from it.



TABLE 4. Determination of Ctr for Styrene using PMMA-SH (SH-content = 0.6%, Mn - 2200) at 70°C. [AIBN] = 1.39 x 10⁻² mol/L

PMMA-SH (g/L)	[SH], mol/L.10 ³	Conversion (%)	Mn	Mw/Mn	Ctr*
10	1.8	15	42120	2.1	3.26 ± 0.39
20	3.6	12	38200	2.3	
30	5.4	10	27500	2.2	
40	6.4	13	23790	2.4	
50	9.0	10	22300	2.2	

* after correction for the molecular weight by PMMA block

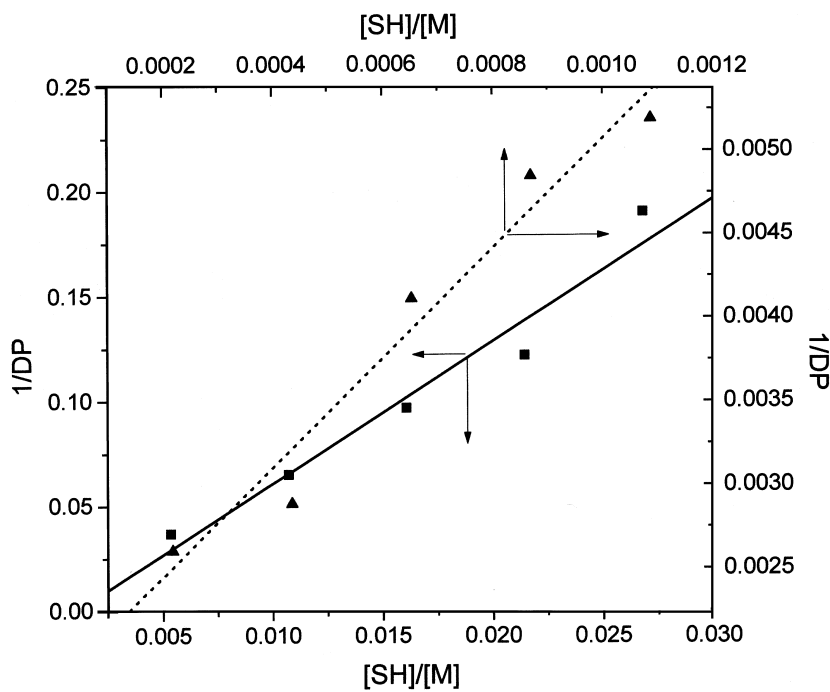


Figure 6. Mayo's plot for determination of Ctr for the pairs, ■ - styrene-HDT, ▲ - styrene-PMMA-SH.

TABLE 5. Synthesis of Block Copolymer using PMMA-SH {Mn- 4600, SH-Content , 0.45%; Mol. Wt. of Active Polymer- 4120}, at 85°C. Polymerization Time - 6 hours

Wt.% of styrene	Wt. % of Macrothiol	Benzoyl peroxide (wt%), $\times 10^3$	Yield (%)	Mn	Mw/Mn	wt.% Carbon	wt.% PMMA	Sequence length of PS	
								obs.	Theor.
75	25	4.0	55	55500	2.1	90.1	7	51380	9170
67	33	2.5	42	46960	2.3	89.4	9	42800	6200
50	50	3.3	40	27200	2.1	87.1	16	23100	3060

Block Copolymer with Fixed PMMA-Sequence Length

In a typical set of experiment, a macrothiol of molecular weight, 4690 with $F_n = 0.45$ was used at varying concentrations for the polymerization of styrene. Details are given in Table 5. The nonfunctional polymers (i.e. type P-P) present in the macrothiol may not interfere with the polymerization and can be removed during the precipitation stage. Due to its presence, the overall molecular weight of the macrothiol does not really represent the length of the active PMMA-SH which finally goes to the block copolymer. This length can be estimated by using the Mayo's equation, knowing the conditions used for synthesizing the macrothiol. The isolated polymers were freed of any unreacted macrothiol by repeated precipitation into methanol-acetone mixture which dissolves out the PMMA-macrothiol. The precipitant was selected by trial precipitation using the macrothiol. It was also ensured that the filtrate does not contain any dissolved block copolymer as evidenced by the absence of UV absorption in GPC of the polymer dissolved in the filtrate. There could be some amount of homopolymer of styrene formed by conventional termination process. This was removed by precipitation of the isolated polymer from its solution in THF into large volume of cyclohexane (or cyclohexane-hexane mixture when percentage of styrene exceeds 75% in the copolymer). The solvent mixture was carefully chosen to avoid extraction of the block copolymer. In fact, this was ensured from the FTIR of the extracted polymer that did not show any evidence for the PMMA polymer. Although this precipitation technique might not ensure exclusive removal of all homopolystyrene, particularly the very high molecular weight ones, the GPC traces of the thus purified polymer did not show any po-



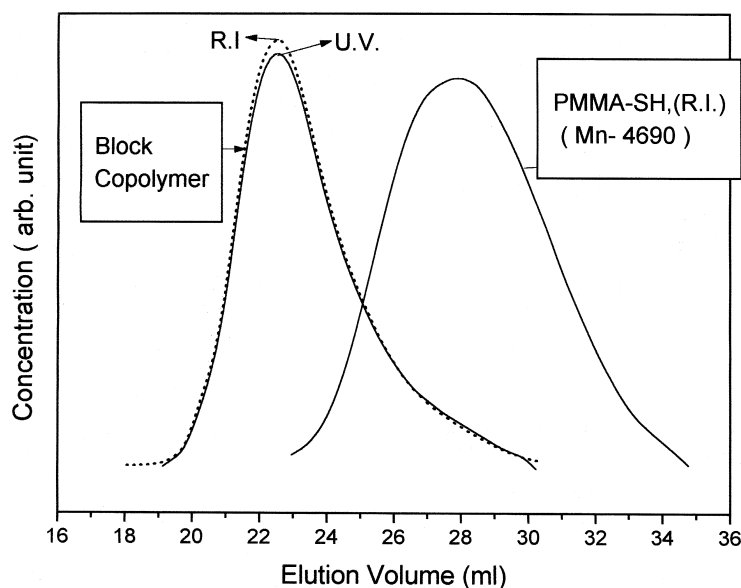


Figure 7. GPC traces of the macrothiol and that of the PMMA-PS diblock copolymer derived from it. Block copolymer properties: Mn- 27200, PMMA-seq. length- 4120, and PMMA- content - 16%.

lymodel distribution that could result from such contaminations. GPC's using UV and RI detectors were superimposable indicating the homogeneity of the copolymer with respect to PMMA blocks. Typical GPC of a block copolymer is shown in Figure 7 along with that of the macrothiol used for its synthesis. It is found that although the length of the styrene sequence decreases with increase in concentration of the macrothiol in the feed, this length is much higher than that estimated by Mayo's equation. This must be arising from the fact that, the high solid-loading for the polymerization done in bulk leads to tremendous increase in the viscosity of the system and as the conversion increases, the transfer reaction involving two polymer chains becomes more diffusion controlled than the propagation. This results in apparent lowering of the C_{tr} values in very viscous systems as the one encountered here. The experimentally determined transfer constant for the macrothiol refers to dilute solution condition (where it is chemically controlled) and does not really represent the actual viscous polymerization system employed for synthesizing the block copolymer.



The copolymer composition could be calculated from the carbon-content and molecular characteristics from GPC. The molecular weight and the overall composition confirm formation of diblock copolymer. The superimposibility of the GPC traces using two detectors (R.I.- sensitive for both PMMA and PS; U.V.- sensitive for PS only) confirmed that the blocks are present in a macromolecule and not as mixture. The theoretical sequence length of the PS calculated based on Mayo's equation and considering the effective concentration of the macrothiol is shown in the same table along with the observed one.

Block Polymer with Varying PMMA- Sequence Length

In another set of experiment, styrene was polymerized in the presence of macrothiols of PMMA of two different molecular weights. The copolymer purification was done as described above. The copolymer characteristics are given in Table 6. As expected, at fixed concentration, the length of polystyrene sequence decreases as the molecular weight of the macrothiol decreases. Here also, the styrene sequences were far longer than theoretically expected for reasons stated above. The superimposibility of RI- and UV-detected GPC of the copolymer implied that they are homogeneous and devoid of homo PMMA. The solvent extraction using hexane-cyclohexane as described above is expected to remove the homo polystyrene. Although the GPC patterns could not confirm absence of homopolystyrene, from the uniform and monomodel GPC pattern it may be to the best approximation concluded that the polymer do not contain homopolystyrene. Diblock nature was confirmed from the molecular characteristic of the copolymer. Block copolymers with macrothiols of still higher molecular weight could not be prepared as in this case, the reaction mixture became very thick and viscous causing the system to gel.

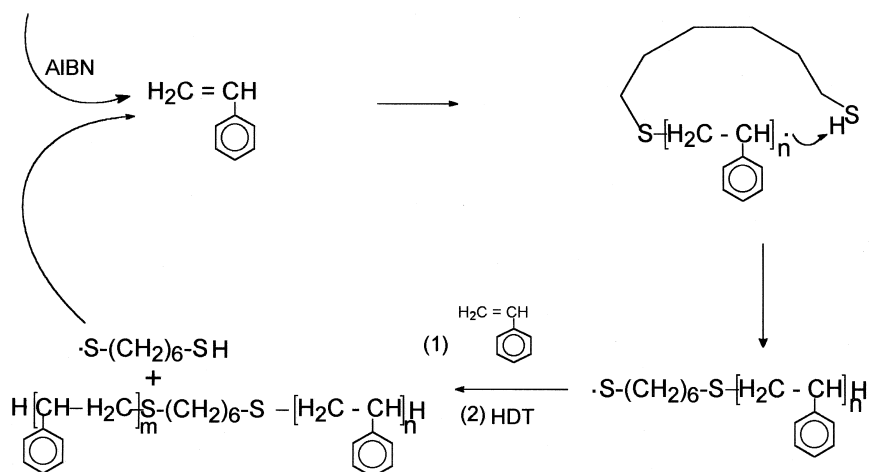
TABLE 6. Synthesis of Diblock Copolymer using PMMA-SH of Varying Mol. Wt. for Polymerization of Styrene. Temperature - 85°C

Mn of PMMA-SH		SH-content (wt.%)	Wt.% of PMMA-SH in feed	yield (%)	Mn copolymer	Mw/Mn	Carbon-content (%)	% PMMA	Sequence length of PS	
actual	effective								Obs.	Thore
6300	4120	0.4	60	55	31850	2.7	88.4	12.1	27730	6280
12300	8560	0.2	50	50	58500	2.6	87.2	15.8	49940	18830

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Scheme 3. Formation of non-functional polymers in styrene/HDT system.

Macrothiols of Other Vinyl Monomers

The syntheses of macrothiols of styrene and butyl acrylate were attempted the same as for MMA. In both cases, the resultant polymer did not possess any mercaptan terminal even at very high loading of the thiol and at very small conversions. In the case of styrene, the polymer formed even at smaller conversion showed bimodal distribution in GPC. The second one at high molecular weight could be attributed to that of polystyrene (PS) formed after rapid exhaustion of the chain transfer agent. Coupling of the formed polymer with I_2 did not absolutely enhance the molecular weight. In these cases, it is quite likely that the chain propagating on one side of hexane dithiol as a result of a preceding transfer, might be getting prematurely terminated by way of transfer to the SH-group on the "tail" of the propagating chain through a kind of "back-biting" reaction. This is shown in Scheme 3. The result is that, once transfer occurs to one SH of a hexane dithiol, transfer to other immediately follows and no polymer can have any SH-terminals. The back-biting normally proceeds when the propagating chain is shorter (so as to form the cyclic transition state) and therefore, the PS-segment on one side hexanedithiol can be expected to be very short when compared to that at the other end.



Although the chain termination could also be caused by the interchain transfer, the probability for that is far less than transfer to the hexane dithiol itself since the latter is present in very high concentration than the former. Moreover, the interchain transfer or transfer of this once reacted polymer radical with hexane dithiol would have left some SH groups in the chain as this would have “spared” the SH-groups in the tail. Since none of these polymers possessed absolutely any mercaptan group, the possibility for the interchain transfer can be, *a priori*, excluded. The absence of mercaptan groups in the formed polymer also rules out the transfer of the once reacted polymer radical with HDT.

Since Ctr in such cases is calculated based on the molecular weight of the formed polymer, the true chain transfer constant is obtained after accounting for this phenomenon. In other words, since each dead polymer chain is caused by two SH- groups of the same molecule, the effectiveness of the chain transfer reaction is only half that in case of normal transfer. This correction has been applied in the estimation of Ctr of styrene using HDT (Table 1). The effective Ctr for the SH- group is only half the apparent Ctr estimated. Interestingly, this value matches with the Ctr of styrene determined using PMMA-SH where no such ambiguity exists.

In the case of butyl acrylate and styrene, this ‘back biting’ phenomenon should be operating. For MMA, probably the α -methyl substituent may be sterically hindering the transition state for such a reaction.

CONCLUSION

Macrothiol of PMMA could be synthesized by the low conversion free radical polymerization of MMA in presence of 1,6-hexane dithiol. For better functionality, it is essential to limit the conversion. The functionality and molecular weight varied with conversion and can be predicted effectively with a kinetic model. The success in the synthesis of macrothiol by this technique is limited to certain monomers. The utility of the macrothiol as macro chain transfer agent in the synthesis of diblock copolymer has been demonstrated. The high solid-loaded polymerization for the block copolymer synthesis however, showed significant deviation from the theoretical prediction based on low viscous systems, due to the effect of diffusion controlled kinetics.



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