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N,*N*′-dipropyl, *N*,*N*′-bis(4-methyl benzene sulfonyl) hydrazide: a new radical source for chain polymerization of vinyl monomers

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Abstract

A new radical initiator *N*,*N*′-dipropyl, *N*,*N*′-bis(4-methyl benzene sulfonyl) hydrazide (DBSH) has been prepared by condensation of *N*-chloro and sodium derivatives of *N*-propyl,4-methyl benzene sulfonamide at room temperature. As a radical initiator DBSH shows interesting properties that, although homolysis of the *N–N* band takes place around 52.5°C, only very low polymerization yields (~1.0 %) are obtained below 100°C. At 100°C, bulk polymerization of methyl methacrylate proceeds rapidly and the reaction is almost quantitative in 2.5 h. This can be attributed to stability of the sulfamidyl radicals to some extent. Radical initiation efficiency of DBSH is about 0.16 and gives high molecular weight of polymers at that temperature. Presence of sulfamidyl groups in polymer chain ends have been confirmed by NMR and elementary analysis.

In the study, for radical initiation ability of DBSH in bulk polymerization of methyl methacrylate and styrene monomers has been investigated in various time, temperature conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Radical initiator; Sulfamidyl radicals; Thermolysis of alkylated ditosyl hydrazide; Homolysis of sulfonyl hydrazides; Polymethyl methacrylate

1. Introduction

Radical generation based on thermal splitting of relatively weak covalent bonds is one of the most common way of radical initiation in vinyl polymerizations. Although many diacyl or dialkyl peroxides and azo compounds have been studied, dibenzoyl peroxide and azo-isobutyronitrile have found common acceptance in practice. Search for new organic radical sources for controlled polymerizations is being current interest by polymer chemists. Disulfides [1] and nitroxides [2] have found much interest as metal-free organic radical sources for controlling polymerizations. Although decomposition of aryl sulfonyl hydrazides yielding nitrogen evolution have been reported [3] there appears only one report dealing with homolitic cleavage of disulphonyl hydrazides yielding sulfamidyl radicals [4]. However, polymerization by sulfamidyl radicals has not been reported yet, presumably due to high bond breaking energy of N–N bonds [5].

We thought that *N*-alkylated sulfonyl hydrazides might be efficient radical sources in combination with suitable activators. Before doing so, in the present study *N*,*N*′-dipropyl, *N*,*N*′-bis(4-methyl benzene sulfonyl) hydrazide (DBSH) has been synthesized and its thermal initiation ability has been tested in bulk polymerization of methyl methacrylate and styrene.

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2. Experimental

The monomers, methyl methacrylate (E-Merck) and styrene (Fluka) were distilled before use. *p*-toluene sulfonyl chloride (Fluka) was recrystallized from chloroform as described in the literature [6]. Propyl amine (Fluka), hydroquinone (E-Merck). All the other chemicals supplied as analytical grade commercial products. These were used without any further purification.

2.1. Synthesis of N,N′-dipropyl, N,N′-bis(4-methyl benzene sulfonyl) hydrazide (DBSH)

This was prepared by three steps of condensation reactions starting from *p*-toluene sulfonyl chloride (Tosyl chloride) and propyl amine. In the first step *N*-propyl, 4-methyl benzene sulfonamide was prepared by reacting *p*-toluene sulfonyl chloride with excess of propyl amine according to the procedure given in the literature [7]. The yield was 96.0%, mp: 52°C (Ref. [8], 52°C).

The sulfonamide obtained was chlorinated with commercial bleaching liquor (45.0% (w/w) NaOCl) according to analog procedure given in the literature [9]. The yield was 94.6%, mp: 44°C.

KOH (29 g, 51.6 mmol) was dissolved in 15 ml methanol. To this solution *N*-propyl,4-methyl benzene sulfonamide (11.0 g, 51.6 mmol) in 20 ml was added *N*-methyl pyrrolidone and stirred for 15 min at room temperature. While stirring the solution of freshly prepared *N*-chloro,*N*-propyl,4-methyl benzene sulfonamide (13 g, 52.5 mmol) in methanol (20 ml) was added in it and the mixture was stirred for 18 h at room temperature. The mixture was poured into 500 ml of cold water and left to stand for overnight. White precipitate was filtered and dried. The yield of crude product was 11.9 g. To purify the crude product it was dissolved in methanol (25 ml) solution containing KOH (3 g) and stirred for 30 min. To this solution were added ether (200 ml) and water (200 ml) in turn and the mixture was transferred in a separatory funnel.

The ether layer separated was dried with $CaCl_2$ (6 g). After filtration about 90% of the ether was removed by airflow. The solution was transferred in beaker and white crystals formed were obtained by filtration. The yield of air-dried product was 2.9 g (13.2 %), mp: 51°C. Elementary analysis: calculated for ($C_{20}H_{28}N_2S_2O_4$), (obtained) C: 56.6% (57.1). H: 6.6% (6.8). N: 6.6% (6.2). ^{1}H-NMR Spectra (with $CDCl_3$, solvent, δ in ppm) : 0.8, t, 3H (CH_3 protons of the propyl group); 1.3–1.6, m, 2H (CH_2 protons adjacent to CH_3 in propyl group); 2.4, s, 3H (CH_3 substituent on phenyl ring); 2.95, t, 2H (N–CH_2–protons); 7.3–7.8, 4H (phenyl ring protons).

Purity of this compound can readily be checked by its FT-IR spectra. Impurity of *N*-propyl,4-methyl benzene sulfonamide exhibits a characteristic sharp peak at 3260 cm^{-1}. Absence of this peak in IR spectra indicates a sufficient purity of the product.

2.2. Polymerization procedure

In order to test radical initiation ability of DBSH bulk polymerization of methyl methacrylate and styrene were studied at different time, temperature conditions and in various initiator concentrations. Respective data collected were used to produce the figures shown in Table 1.

3. Results and discussion

DBSH was synthesized by condensation of *N*-chloro and sodium derivatives of *N*-propyl,4-methyl benzene sulfonamide as shown in the reaction sequences above (Scheme 1).

Since the elementary composition of DBSH does not differ from those of the starting compound, *N*-propyl,4-methyl benzene sulfonamide, elementary microanalysis gives no further information about formation of the DBSH. The structure of this compound is clearly evidenced by its ^{1}H-NMR spectra.

Table 1
Yields and molecular weights in bulk polymerization of MMA at various initiator concentrations

Run	I_0/M_0[a]	Polymerization yield (%)[b]	Viscosity[c]	M_v[d]	M_w/M_n[e]	Initiator efficiency
1	5.04×10^{-3}	45.4	1.23	898 000	1.43	0.156
2	10.9×10^{-3}	67.7	0.99	654 000	1.46	0.160
3	15.8×10^{-3}	92	0.86	536 000	1.52	0.173
4	25.2×10^{-3}	99.7	0.72	411 000	1.46	0.150

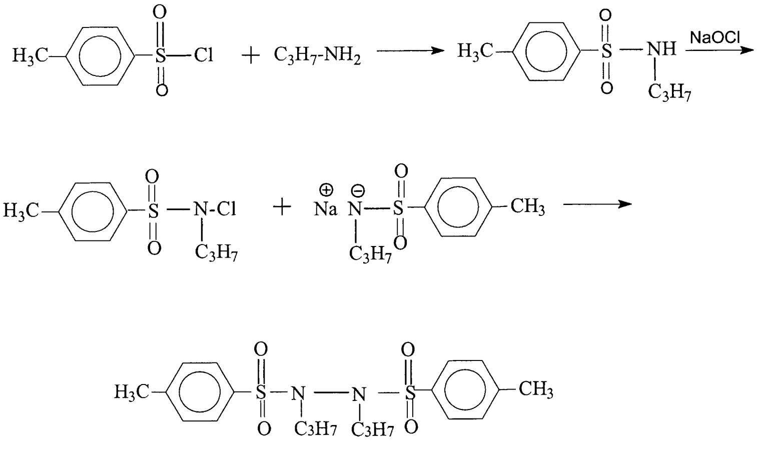
[a] Molar ratio of the initiator to MMA.

[b] At 100°C for 2 h.

[c] In toluene (at 30°C, 0.1 g dl^{-1} conc.).

[d] Viscosity av. mol. wt.

[e] By GPC using THF solvent and polystyrene as standard.



(DBSH)

Scheme 1.

Thus, absence of N–H protons at 4.7 ppm observed in sulfonamides indicates that the compound is free of the impurity arising from unreacted *N*-propyl,4-methyl benzene sulfonamide.

Also in its FT-IR spectra NH stretching and bending vibrations of the starting compound (observed at 3260 and 1610 $\mathrm{cm^{-1}}$) do not appear, which indicates purity of the product.

Thermal decomposition of DBSH was studied by differential scanning calorimetry (DSC). The DSC thermogram in Fig. 1 gives a single endothermic peak at 52.5°C, which corresponds melting and homolysis of DBSH.

In a separate experiment melting temperature of the compound was found to be 51°C. Homolytic cleavage and melting occur simultaneously. This result is in accordance with many homolitically cleavable compounds such as dialkyl and diacyl peroxides. The peak at 52.2°C gives a total $\Delta H = 22.8\ \mathrm{kJ\,mol^{-1}}$ enthalpy change for melting and decomposition.

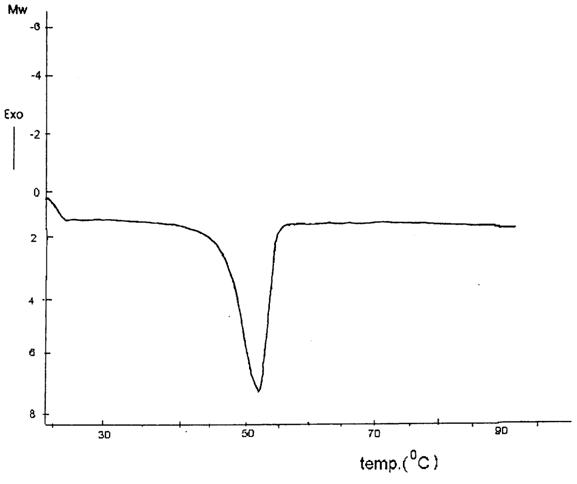


Fig. 1. DSC traces of crystalline DBSH (heating rate 5°C/min).

It is interesting to note that cooling curve exhibits the same peak. Reversibility of the peak indicates that two radicals form on heating and recombine on cooling, without side reactions.

We have intended to study the decomposition kinetics of DBSH colorimetrically using TEMPO in t-butanol. However, no marked difference was observed in UV-spectra of DBSH-TEMPO mixtures.

In this study the decomposition kinetics was followed by an alternative procedure using hydroquinone as radical scavenger.

Hydroquinone itself has two absorption maxima at 232 and 295 nm ($\varepsilon = 2786$). In presence of DBSH the later decrease in time and a new band emerges at 282 nm. We have assumed that intensity of the new band should be proportional to decrease in the intensity of the band at 295 nm wavelength. Absorbance at this wavelength at any time,

$$A = \varepsilon_1(a - x)l + \varepsilon_2 xl$$

ε_2 denotes molar absorption coefficient of the entity leading to the new band at 295 nm. *a* the initial concentration of the hydroquinone. The second term represents contribution from tale absorption of the new band.

By rearranging the above equation, we get

$$x = \frac{\varepsilon_1 al - A}{(\varepsilon_1 - \varepsilon_2)l}$$

Since $\varepsilon_1 al$ is equal to the band intensity arising from hydroquinone itself at the beginning, A_0 and the denominator term is constant. By taking logarithm,

$$\ln x = \ln(A_0 - A) - \text{constant}$$

Hence a plot of $\ln(A_0 - A)$ versus time gives first order plot for decomposition of DDH. From the slope of the straight line (correlation factor 0.902) rate constant for the decomposition at 60°C was found to be $k = (8.1 \pm 0.6) \times 10^{-4}$ s^{-1}. By measuring the rate constants at 50°C, 60°C and 68°C the Arrhenius plot gives 12 ± 1.4 kcal mol^{-1} of activation energy which is rather small in comparison to those of diacyl peroxides.

3.1. Bulk polymerization with DBSH as initiator

Initiation ability of DBSH was tested in bulk polymerization of methyl methacrylate and styrene monomers. Although radical forming temperature is about 50°C only low polymerization yields are obtained at the temperature below 100°C (Fig. 2).

This behavior can be attributed to low reactivity of the sulfamidyl radicals towards the monomers. Another reason of the low reactivity might be stability of the radicals. We have assumed that at 100°C the initiation takes place via sulfamidyl radicals as shown in Scheme 2.

In order to prove the initiation through sulfamidyl radicals a separate experiment was performed using excess of the initiator ($[I]/[M] = 1/20$). To remove unreacted initiator, the resulting polymer was dissolved in acetone and reprecipitated in methanol. ^{1}H-NMR spectrum of the polymer (Fig. 3) clearly represents weak aromatic proton signals in 7.2–7.7 ppm range. Integral ratio of that signal to those of methoxy protons of the monomer at 3.6 ppm indicates about 9500 Daltons of molecular weight.

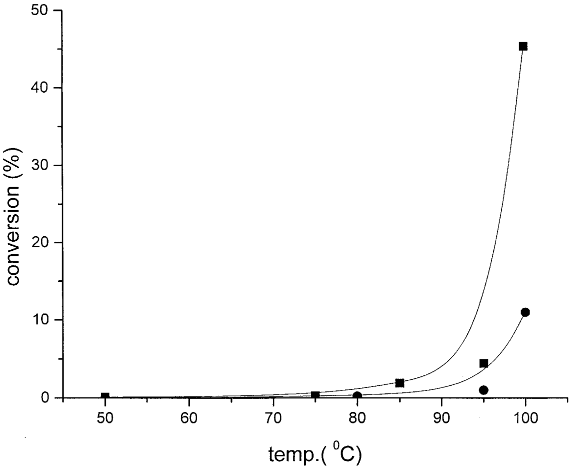
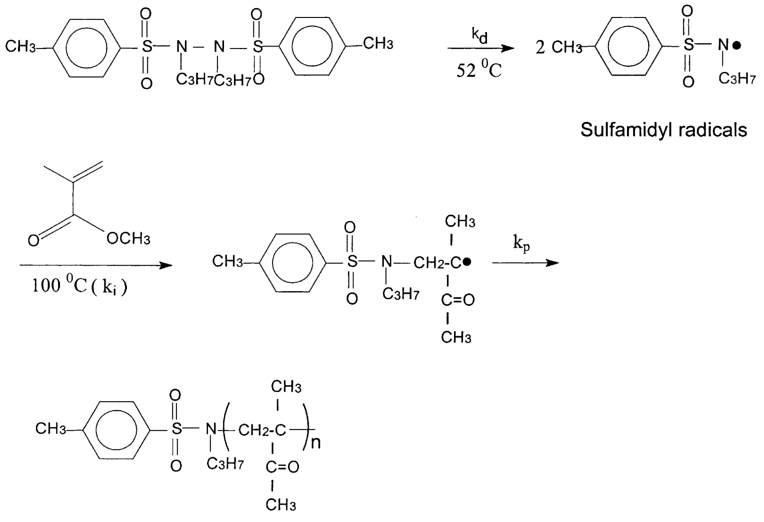


Fig. 2. Polymerization yields of (■) MMA and (●) styrene at various temperatures in 2 h.

Another evidence of the sulfamidyl end group is elementary microanalysis of the polymer sample. 0.17% of nitrogen content approximately matches with the above estimation based on the ^{1}H-NMR spectrum. Obviously molecular weight of the sample is higher than expected which implies relatively low initiation efficiency of the initiator.

Since termination of MMA polymerization by combination is negligible, initiation efficiency of the initiator can be estimated based on yield and number-average molecular weights as usual. Using data in Table 1 average initiation efficiency of the initiator is found as 0.16



Scheme 2.

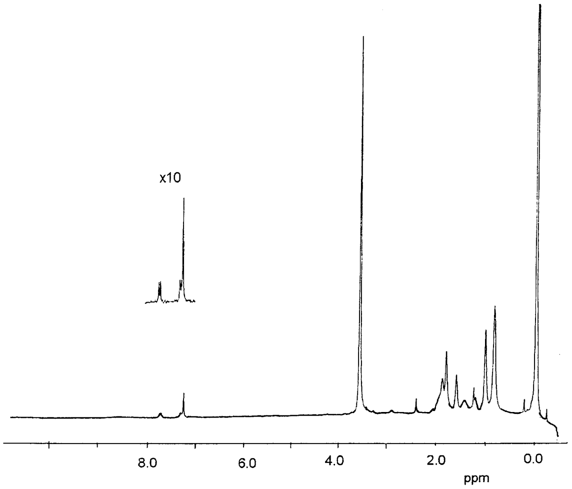


Fig. 3. ^{1}H-NMR spectra of polymethyl methacrylate (with $[I]/[M]$:1/20 molar ratio).

(at 100°C) which is rather small, in comparison to those of common peroxide initiators.

Viscosity-average molecular weights of the polymers obtained are reasonably high even at earlier stages of conversions. This can be ascribed to the low initiation efficiency.

As it would be expected conversions of MMA and styrene polymerization gradually increase in time (Fig. 4). Polymerization of MMA takes place almost quantitatively in 2.5 h at that temperature. However, comparing with MMA polymerization of styrene is somewhat slower.

In conclusion, polymerization of vinyl monomers by sulfamidyl radicals resulting from thermal cleavage of N–N linkages in DBSH is possible at 100°C. Initiation efficiency of DBSH is around 0.16 at that temperature. Regarding with its low initiation efficiency and high polymerization temperature there is no any apparent advantage over common radical initiators. But the results obtained show possibility of radical initiation by sulfamidyl radicals.

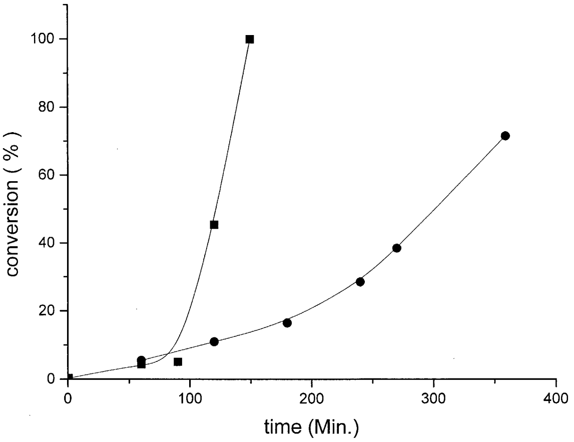


Fig. 4. Conversion–time plots in polymerization (■) MMA and (●) styrene at 100°C (4.72 × 10^{-2} M, initiator concentration).

Obviously this first example on polymerization by the sulfonyl hydrazide, DBSH needs further investigations directed towards preparing additional derivatives to obtain easily cleavable new initiators.

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