ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 12073–12080

polymer

www.elsevier.com/locate/polymer

Synthesis, characterisation and decomposition of 1,3-benzene disulfonyl azide; a cross-linking agent for polyolefins

Jens Kjær Jørgensen [a,*], Espen Ommundsen [b], Aage Stori [c], Keith Redford [c]

[a] Department of Engineering and Design Materials, Norwegian University of Science and Technology,
Richard Birkelandsvei 2b, 7491 Trondheim, Norway
[b] SINTEF Materials and Chemistry, Pb. 124 Blindern, 0314 Oslo, Norway
[c] Borealis AS, N-3960 Stathelle, Norway

Received 28 February 2005; received in revised form 12 October 2005; accepted 14 October 2005
Available online 4 November 2005

Abstract

We have studied the thermal decomposition of 1,3-benzenedisulfonyl azide (1,3-BDSA), and verified that sulfonyl nitrenes formed are able to cross-link polyolefins, including PP. The decomposition was studied with DSC, TGA, and the GC–MS analysis of gaseous products. Both the decomposition of pure 1,3-BDSA and 1,3-BDSA dissolved in a polyolefin were studied. Decomposition occurs by loss of nitrogen giving sulfonyl nitrenes. In the polyolefin nitrenes cross-links the carbon chains by C–H insertion. Cross-linking of PP was verified with SEC. SEC showed no signs of decomposition of PP. Decomposition in the polyolefin was a first order reaction with a half-life of 25.7 s at 200 °C. Hence, 1,3-BDSA is suited for processing with polyolefins. Decomposition of pure 1,3-BDSA is more complicated with unwanted products such as SO_2 and benzene being formed, thereby emphasising the need for good blending when used in polyolefins.

Keywords: Cross-linking; Sulfonyl azides; Polyolefins

1. Introduction

Disulfonyl azides have earlier been shown to be effective agents for cross-linking of various hydrocarbon polymers [1–7]. The cross-linking reaction between hydrocarbons and sulfonyl azides are believed not to involve radicals, but to occur by an insertion reaction. Disulfonyl azides are, therefore, capable of cross-linking polyolefins with tertiary carbon atoms, such as polypropylene and polyethylene copolymers. Tertiary carbon containing polymers are exposed to chain scission in the presence of free radicals. Free radical based method used for polyethylene such as peroxides and radiation are, therefore, except in some special cases [8], unsuited for cross-linking of polypropylene and polyethylene copolymers.

In this paper we consider the synthesis and characterisation of 1,3-benzenedisulfonyl azide (1,3-BDSA) (Fig. 1). 1,3-BDSA is intended to be used for cross-linking of polyolefins. We also include a study of the decomposition kinetics of 1,3-BDSA dissolved/blended in a polyolefin. Finally we have processed PP with 1,3-BDSA and used size exclusion chromatography to verify that cross-linking occurs. The purpose of the decomposition analysis is to get a reliable basis for estimation of process curing times. To our knowledge the kinetics of thermal decomposition of sulfonyl azides dissolved in a hydrocarbon polymer has not earlier been addressed in the literature. In two following papers [9,10] we explore in more details the capability of 1,3-BDSA to introduce long-chain branching (LCB) in polyethylene and polypropylene, and the impact of these LCB on rheological properties.

1.1. Synthesis of 1,3-BDSA

Curtius et al. were the first to describe the synthesis of 1,3-benzenedisulfonyl azide (1,3-BDSA) [11]. The synthesis of a vast number of other mono- and disulfonyl azides has been reviewed by Breslow [12] some years ago. Recently Baker et al. described the synthesis of a number of disulfonyl azides intended for cross-linking, and also included a detailed characterisation with spectroscopic methods [13].

1,3-BDSA is easily synthesised from 1,3-bezenedisulfonyl chloride and sodium azide by the Forster–Fiertz reaction (Scheme 1) giving 1,3-BDSA and sodium chloride [12]. The

---

[*] Corresponding author. Present Address: SINTEF Materials and Chemistry, Pb. 124 Blindern, 0314 Oslo, Norway.
E-mail address: jens.k.jorgensen@sintef.no (J.K. Jørgensen).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.077

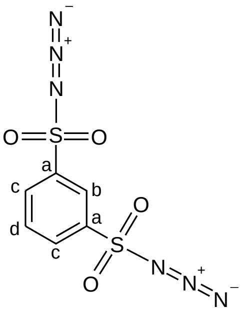
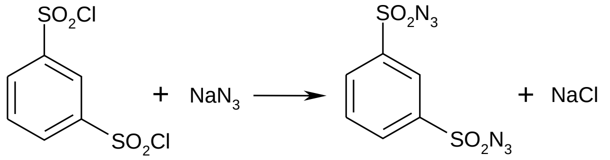


Fig. 1. Chemical structure of 1,3-benzenedisulfonyl azide.

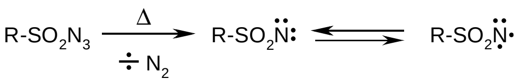
Forster–Fietz reaction involves addition of an acetone (or ethanolic aqueous) solution of a sulfonyl chloride to a cold saturated aqueous solution of sodium azide. This must be done with efficient stirring. Both reactants can be purchased from several suppliers. 1,3-Bezenedisulfonyl chloride can also be prepared from 1,3-benzenedisulfonic acid [13].



Scheme 1. Synthesis of 1,3-BDSA due to the Forster–Fiertz reaction.

1.2. Decomposition of sulfonyl azides and reactions with hydrocarbons

For the purpose of cross-linking of hydrocarbons with disulfonyl azides it is important to know the decomposition kinetics of the disulfonyl azide in the actual type of hydrocarbon. Decomposition of sulfonyl azides in different organic solvents has been studied in details by Breslow et al. [14]. Breslow found that the reactions and kinetics of different sulfonyl azides are similar when dissolved in the same hydrocarbon. On the other hand a study on photo decomposition in different hydrocarbon matrixes (oils and polymers) by Reiser et al. [15] showed significant differences in reaction paths and rates for the same azide in different hydrocarbons. This is caused by differences in hydrocarbon mobilities. Rate constants reported in those earlier papers cannot necessarily be used as basis for calculation of curing times in polyolefin materials. To compensate for this lack of data we investigated the reaction kinetics of thermal decomposition of 1,3-BDSA in a polyolefin melt.



$$R\text{-}SO_2N_3 \xrightarrow[\div N_2]{\Delta} R\text{-}SO_2\ddot{N}\colon \rightleftarrows R\text{-}SO_2\ddot{N}\cdot$$

Scheme 2. Formation of singlet and triplet nitrenes from azide.

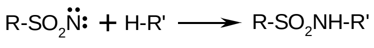
At elevated temperatures sulfonyl azides decompose to form a sulfonyl nitrene as shown in reaction Scheme 2. The nitrene exist in both the singlet and the triplet state. Both states can react with hydrocarbons but they do it in different ways. The reaction involving the singlet nitrene is an insertion at the C–H bond giving a secondary sulfonamide (Scheme 3). The triplet nitrene reacts by abstraction of a proton from the hydrocarbon resulting in the formation of a macroradical (Scheme 4(a)). This reaction can be followed either by a recombination of the two products to form the same product as in (Schemes 3 and 4(b)), or by abstraction of second proton from another hydrocarbon to give a primary sulfonamide (Scheme 4(c)). Whether recombination or a second abstraction will occur depends on the mobility of the hydrocarbon. The amount of recombination decreases as the mobility of the hydrocarbon increases [15]. Since polymers have low mobility we expect recombination to be dominant. If a second H-abstraction occurs it results in two macroradicals that can combine with other radicals or be involved in chain transfer reaction or reactions leading to chain scission. The reactions shown here involving nitrenes are extremely fast. Thus, the rate-determining step is the nitrene formation. The decomposition due to these reaction paths has been found to be a first-order reaction [14]. For the purpose of cross-linking the reactions of Schemes 3 and 4(a) and (b) or (a) and (c) followed by macroradical recombination, have to occur.

Another possibility is loss of the whole sulfonyl azide group with formation of SO_2. This has been observed during thermal decomposition of different sulfonyl azides in mineral oil and organic solvents [14]. The formation of SO_2 makes the reaction order as seen from gas evolution deviate from one. This deviation is observed only after a certain extent of reaction (at least 1 halve life), and is inhibited in presence of a radical trap antioxidant. These observations suggest that the formation of SO_2 is in some way catalysed by nitrenes or substances formed in reactions involving nitrenes. They also suggest that the reaction is involving radicals although a specific origin of the radical has not been determined and could be dependent of the system (possible radical sources are nitrenes in the triplet state, and in polymers macroradicals formed by reaction with nitrenes or from mechanical or thermal cleavage). There are many puzzling features about the SO_2 formation that have not been clarified. Scheme 5 shows one suggested reaction path [14]. Effective suppression of reactions leading to loss of sulphur dioxide would be indicated by a decomposition of the sulfonyl azide that follows first order kinetics. The presence of antioxidant also lowered the reaction rate to nearly the half. This indicates that also the nitrene formation is accelerated by radicals.

It is also important that oxygen is not present since it easily reacts with nitrenes to form a nitroso compound (Scheme 6) [16]. Other unwanted reactions are formation of azo dimers from two nitrenes or from a nitrene and an azide (Scheme 7). The reactions of Scheme 7 will be more likely to occur in a pure sulfonyl azide or in highly concentrated solution.

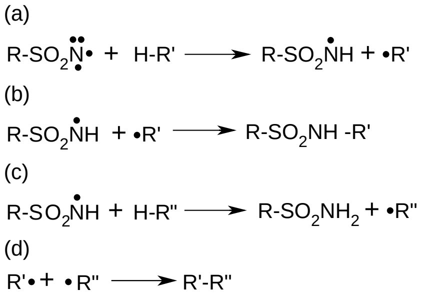
1.3. Kinetic measurements

The decomposition kinetics of sulfonyl azides can be studied by capture and analysis of the gas formed in the



$$R\text{-}SO_2\ddot{N}\colon + H\text{-}R' \longrightarrow R\text{-}SO_2NH\text{-}R'$$

Scheme 3. Reaction of singlet nitrene with hydrocarbon. Formation of secondary sulfonamide.



Scheme 4. Reaction of triplet nitrene with hydrocarbon. (a) H-abstraction, (b) formation of secondary sulfonamide by recombination, (c) formation of primary sulfonamide by abstraction of a second proton, (d) combination of macroradicals formed by reaction (b) and (c), mechanical cleavage or in other ways.

decomposition (nitrogen and sulphur dioxide). A more readily method is differential scanning calorimetry (DSC) though it does not give exact information of the decomposition products. DSC can be performed isothermally or at a controlled temperature rate. As discussed in the experimental section we have utilised a constant temperature rate. The kinetic parameters can be found from the shape of the peak of a single temperature scan by fitting of the data to an appropriate model. Below we give a summary of the basis for our analysis, detailed discussions on the subject is found elsewhere [17,18].

For chemical reactions the rate of conversion can often be described by the equation

$$\frac{d\alpha}{dt} = k(1-\alpha)^n, \tag{1}$$

where α is the degree of conversion, t is the time and n the reaction order. k is a rate constant described by the Arrhenius equation

$$k = A\,\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

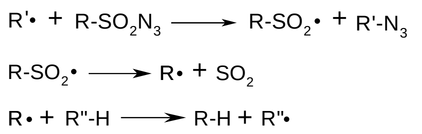
E_a is the activation energy, R the gas constant, T the temperature and A a pre-exponential factor. For a constant temperature change Eqs. (1) and (2) can be combined to

$$\frac{d\alpha}{dT} = \beta A\,\exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \tag{3}$$

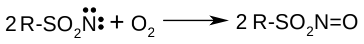
where $\beta = dt/dT =$ consant.

If a DSC-peak represents a conversion with temperature independent molar enthalpy, then $d\alpha/dT$ is proportional to the DSC-signal and $\alpha(T)$ is found by integration. This is not the case if the peak represents a combination of reactions with different temperature dependence. From $d\alpha/dT$ and $\alpha(T)$, E_a, n and A is found from non-linear regression by minimising the sum

$$\sum_{i=1}^{m}\left(\left[\frac{d\alpha}{dT}\right]_i - A\exp\left(-\frac{E_a}{RT_i}\right)(1-\alpha_i)^n\right)^2 \tag{4}$$



Scheme 5. Loss of the sulfonyl azide group due to a radical initiated reaction path.



Scheme 6. Reaction of sulfonyl nitrenes with oxygen.

To verify the assumption that $d\alpha/dT$ is proportional to the signal and the model valid, a theoretical reaction peak $d\alpha/dT_{\mathrm{model}}$ is found from the numerical solution of Eq. (3) with E_a, n and A found in the regression. Significant difference between the two sets of $d\alpha/dT$ would invalidate the results.

For the kinetics described above the half-life is given by

$$t_{1/2} = \frac{1}{1-n}\left(1-\left(\frac{1}{2}\right)^{1-n}\right)\frac{1}{k} \tag{5}$$

2. Experimental

2.1. Synthesis of 1,3-benzedisulfonyl azide

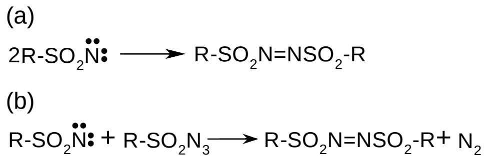
1,3-Benzenedisulfonyl chloride (20 g, 0.07 mol) in acetone (120 mL) was added drop wise to a solution of sodium azide (9.5 g, 0.14 mol) in water (40 mL) at 0 °C. Upon addition of half of the solution a white precipitate was seen. After stirring for 1 h at <5 °C the precipitate was filtered off and the solid washed with cold water to yield the 1,3-benzedisulfonyl azide as a white solid (20.5 g, 98%). (NB azides can be destroyed in a careful manner by the addition of sodium thiosulfate and iodine).

2.2. Compounding

All polymer melt blending and reactive extrusion were performed in a DSM2000 extruder. DSM2000 is a 15 cm^3 twin screw extruder with feedback that gives good blending with low mechanical degradation of small batches. The DSM2000 is a closed unit, where the melt is circulating. It is emptied through a die that the operator opens after the desired processing time. Emptying takes approximately one minute. Consequently the processing time of different parts of a batch can vary by up to 1 min.

2.3. Reactive extrusion of PP with 1,3-BDSA and dicumyl peroxide

We modified a linear isotactic homopolymer PP supplied by Borealis AS by reactive extrusion with 2000 ppm 1,3-BDSA.



Scheme 7. Formation of azo dimmer by (a) dimerization of sulfonyl nitrenes or (b) attack of sulfonyl nitrene on sulfonyl azide.

For comparison with a process involving radicals we modified the same PP with 2000 ppm dicumyl peroxide (DCP). The PP was supplied as unstabilised reactor powder. Reactor powder is preferred to pellets since it has larger surface making blending with the modifiers easier. 1,3-BDSA and DCP have molecular weight 288 and 270 g/mol, respectively. 2000 ppm of both thus corresponds to approximately the same molar amount. The PP was stabilised with 800 ppm Irganox 1010, 1200 ppm Irganox 168 and 900 ppm Ca-stearate. Both 1,3-BDSA and DCP were dissolved in acetone and the solution was blended into the PP. After evaporation of the acetone the blend was extruded for 5 min at 200 °C in the DSM2000.

2.4. NMR and FTIR

Proton and ^{13}C nuclear magnetic resonance spectroscopy were performed on a Varian Gemini 2000–300 MHz NMR spectrometer with deuterated dimethyl sulfoxide (DMSO) as solvent and tetramethylsilane (TMF) as standard. Fourier transform infrared spectra were obtained on a Perkin–Elmer System 2000 FTIR with the sample dispersed in KBR.

2.5. DSC

DSC analyses were performed on a Perkin–Elmer Pyris Dynamic DSC at heating rate 20 °C/min, and with nitrogen as purge gas. DSC analysis were carried out on both pure 1,3-BDSA and 5000 ppm 1,3-BDSA in a polyolefin. 5000 ppm was chosen to have enough material to give a useful signal but still at a concentration low enough to avoid clusters of azide in the matrix.

5000 ppm was not a high enough concentration to do isothermal calorimetric measurement. A satisfactory signal could be obtained by analysing at high temperature, but in that case the reaction rate was too high to reach a stable temperature, before nearly full conversion was achieved. Our choice was, therefore, to make temperature scans and analyse as described above.

To make it possible to measure the decomposition kinetics of 1,3-BDSA dissolved in polyolefins, one needs a polyolefin with melt and processing temperature well below the decomposition temperature of 1,3-BDSA. For this purpose we used the PE copolymer Dow Affinity SQ1503 UE. Dow Plastics report a melting point of 97 °C for SQ1503. In DSC analysis at heating rate 20 °C/min the melting peak ended at 107 °C. SQ1503 was stabilised by the manufacturer. Three batches of SQ1503 with approximately 5000 ppm 1,3-BDSA were prepared by dissolving 55 mg of 1,3-BDSA in acetone and blending it thoroughly into powder of SQ1503. After evaporation of the acetone the blends were extruded in the DSM2000 extruder for 3 min at 110 °C and 50 rpm.

2.6. Thermogravimetric analysis (TGA)

TGA was performed with a Perkin–Elmer TGA 7 at heating rate 20 °C/min, and with nitrogen as purge gas. The expected weight loss of the PE/1,3-BDSA blends are approximately 0.1%. Measurements on the blends would, therefore, be invalidated by evaporation of even small amount of moisture or other substances in the polymer. TGA analysis was, therefore, performed only on pure 1,3-BDSA.

2.7. GC–MS

GC–MS analyses were performed to analyse the gaseous reaction products of the decomposition of 1,3-BDSA. The instrument used was a Varian 3400 GC interfaced with a Thermo Finnigan ITS 40 ion trap mass spectrometer. The instrument set-up was as follows: sample introduction: head-space, 0.5 mL. Split/splitless injection, ratio 1:20. Injector temperature: 280 °C. Carrier gas: He, 1 ml/min. Separation: J and W DB 624 fused silica capillary column (30 m × 0.25 mm × 1.8 μm). Oven programming: $-20 \rightarrow 10(5) - 6 - 120(0) - 10 - 240(5)$. Transfer line; 350 °C. Mass spectrometer operation: full scan, 29–250 amu, 1 scan/s

As for DSC GC–MS was performed on both pure 1,3-BDSA and 5000 ppm blends of 1,3-BDSA and PE. In the case of pure 1,3-BDSA approximately 2 mg was weighted into a 40 mL septum topped VOA vial. The vial was then flushed with argon to remove nitrogen and oxygen. Decomposition was carried out by heating the vial at 200 °C in a ventilated oven for 3 min. During the 3 min the white 1,3-BDSA powder became charred. A sample of 0.5 mL of the evolved gas was removed from the vial atmosphere with a preheated airtight syringe and injected into the GC. Analysis of the 5000 ppm PE/1.3-BDSA blend was carried out in similar way with 400 mg blend corresponding to 2 mg 1,3-BDSA. To shorten the diffusion path of the gaseous reaction products out from the PE-melt we used thin films pressed at 110 °C. Due to the extra heat required to warm up and melt the blends they were heated for 10 min at 200 °C. During those 10 min the blend melted and vapour bubbles became clearly visible.

2.8. Size exclusion chromatography (SEC)

SEC analyses were performed using a Polymer Laboratories GPC 210 equipped with a PL differential refractometer (DRI). The columns used were a set of four Plgel 20 μm MIXED-A LS 300 × 7.5 mm and a Plgel 20 μm Guard 300 × 7.5 mm.

The analyses were performed at 145 °C with a flow rate of 1.00 mL/min and 1,2,4-trichlorobenzene (TCB) stabilized with 0.02 wt% 2,6-di-*tert*-butyl-*p*-cresol (BHT) as solvent. Samples for SEC were prepared by dissolving an accurate amount of approximately 20 mg sample in 20 mL of 1,2,4-trichlorobenzene (TCB) stabilized with 0.02 wt% 2,6-di-*tert*-butyl-*p*-cresol (BHT). Dissolution of the samples was achieved in an oven at 160 °C for 1.5 h. The PP used contains catalyst residues. To avoid column frit blockage (10 μm column fit) from these particles all samples were filtered at 145 °C with hot filtration device consisting of a syringe and filter in a heated block. The filters used were 5 μm MITEX PTFE discs from Millipore contained in a Swinney stainless filter holder.

Table 1
Proton and carbon 13 NMR data of 1,3-benzenedisulfonyl azide in DMSO with TMS as reference

Chemical shift (ppm)				
Position	*a*	*b*	*c*	*d*
H	–	8.41 (t, *J* = 1.8 Hz, 1H)	8.50 (dd, *J* = 7.9, 1.8 Hz, 2H)	8.10 (t, *J* = 7.9 Hz, 1H)
^{13}C	139.23	132.72	133.64	125.70

Positions refer to Fig. 1.

3. Results

FTIR and NMR analyses of the product gave results in excellent agreement with values reported by Baker et al. for 1, 3-BDSA [13]. The only notable difference is that we have a higher resolution in the NMR measurement resulting in a more detailed splitting pattern. NMR data are listed in Table 1. The FTIR spectra showed strong absorbance at 2142/cm confirming the presence of the sulfonyl azide group.

GC–MS analysis showed clearly that SO_2 is a product of the decomposition of pure 1,3-BDSA. We also detected small amounts of benzene. Benzene is the product if both sulfonyl groups are lost due to Scheme 5. In the gaseous reaction product from PE/1,3-BDSA blends we found no trace of SO_2 or benzene. Instead we found traces of various compounds that we assume are residues from synthesis of the PE or products formed from additives in the PE. From visual and physical inspection of the PE/1,3-BDSA after the heating procedure, we find it unlikely that absence of SO_2 in the analysis should be due to encapsulation in the polymer.

TGA showed a sharp decomposition starting at 170 °C. The weight loss at 250 °C was 32.5% (Fig. 6). The same result was obtained by Baker et al. [13]. This is more than the 20% weight loss expected by decomposition to nitrenes exclusively. The extra weight loss is due to the formation of SO_2 and benzene as we observed in GC–MS analysis.

Results from DSC analysis are shown in Figs. 2–5 and Table 2. Fig. 2 shows the DSC trace of 1,3-BDSA. The curve has a distinct endothermic melting peak with onset at 85 °C followed by a large exothermic peak with onset at 127 °C due to decomposition. We were not able to locate the melting peak on the blends of 1,3-BDSA and polyethylene. We interpret this as that the azide is dissolved or very well dispersed in the polymer. This is important for the purpose of cross-linking, where an even distribution of cross-linker is desired. Fig. 3 compares the calculated conversion rates of 1,3-BDSA and the blend with polyethylene. The peaks are similar in shape but the decomposition in polyethylene takes place approximately 10 °C above the decomposition in pure form. Kinetic parameters obtained from analyses of the DSC data are listed in Table 2. The regression curves due to Eq. (4) and the solutions of Eq. (3) are shown together with the measured data in Figs. 4 and 5. The model data fit the measured data excellently for the azide and good for the blend.

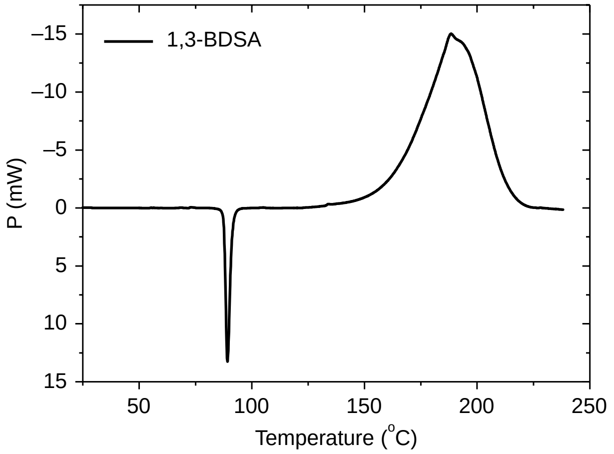


Fig. 2. DSC curve of pure 1,3-benzenedisulfonyl azide. Heating rate 20 °C/min.

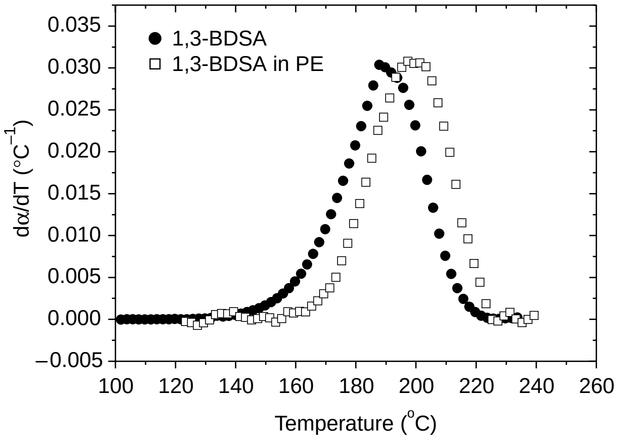


Fig. 3. Comparison of conversion rates of 1,3-benzenedisulfonyl azide in pure form and in 5000 ppm solution in polyethylene. Values are calculated from DSC peaks obtained with heating rate 20 °C/min.

As a reference for the use of 1,3-BDSA as cross-linker we have calculated half-lives and time required for 99.8% conversion (nine times the half-life), at various temperatures

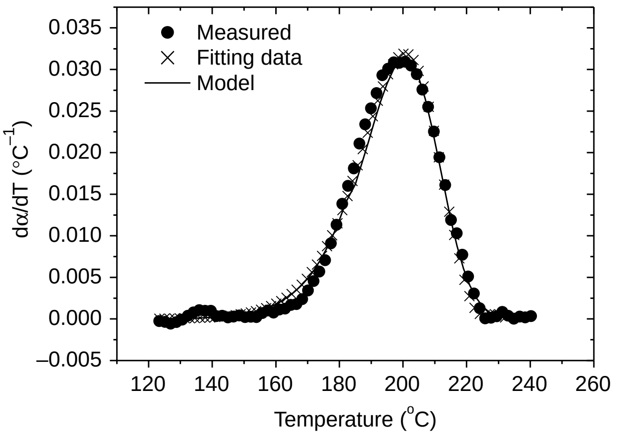


Fig. 4. Conversion rate of 5000 ppm 1,3-benzenedisulfonyl azide in polyethylene. Heating rate 20 °C/min. The data set is and average of four runs. Measured and Fitting data are the first and second term in Eq. (4), respectively. Model is the solution of Eq. (3).

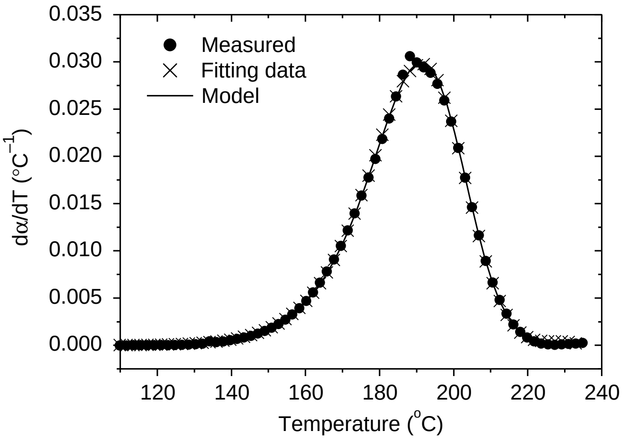


Fig. 5. Conversion rate of pure 1,3-benzenedisulfonyl azide. Heating rate 20 °C/min. Measured and Fitting data are the first and second term in Eq. (4), respectively. Model is the solution of Eq. (3).

Table 3. One should bear in mind that these values are based on model data, and probably are most reliable at temperature around 200 °C, where the experimental data used in the regression are of best quality. Though the viscosities of polyolefin melts are highly dependent of molecular weight and branching structure, chain motions on scales comparable to the size of 1,3-BDSA are similar. We, therefore, expect these results to be valid in all polyolefins.

SEC results of PP modified with 2000 ppm 1,3-BDSA and 2000 ppm DCP are compared to the trace of the unmodified PP in Fig. 7. The data shown are baseline subtracted concentration data normalized to area one as a function of retention volume V_e. In SEC fractions of the same molecular weight elutes at the same V_e, and V_e increases with decreasing molecular weight. The results show that a high molecular weight fraction is formed in PP modified with 1,3-BDSA. At the same time there are no sign of an increase of low molecular fractions. On the other hand the treatment with peroxide that generates macroradicals clearly results in chain scission and shift of the whole peak to lower molecular weights.

4. Discussion

From the SEC results it is apparent that 1,3-BDSA is capable of cross-linking PP. Also the formation of triplet nitrenes, and thereafter proton abstraction giving macroradicals (Scheme 4(a)) that results in chain scission, is minimal.

There are notable aspects of the kinetic results that give rise to discussion. Decomposition of 1,3-BDSA in pure form and in polyethylene has the same reaction order, and the order is very close to one. At the same time the decomposition in polyethylene has lower rate constant and lower molar reaction enthalpy. Since the reaction orders are close to one they suggest that the rate determining step is the formation of 1,3-benzenedisulfonyl nitrene (Scheme 2), and that it dominates decomposition with loss of the sulfonyl group (Scheme 5). The reaction order is the same in the two cases implying that the rate determining steps are the same. If we compare our findings to values reported for *p*-toluene sulfonyl azide in tetradecane in a thermal decomposition with first order kinetics and low SO_2 formation [14] (Table 2), we find that they are in agreement with the values we obtain for 1,3-BDSA/PE blends.

An explanation for the lower reaction rate in polyethylene could be that the nitrene formation is submitted to a cage effect, as is well known to occur for peroxides [19]. A reason we find more likely is that the free electrons of triplet nitrenes, or radicals produced from reactions between nitrenes or between nitrenes and impurities could catalyse the decomposition, as discussed above. In that connection it is noteworthy that the polyethylene used in the blends was stabilized.

The difference in reaction enthalpy and the fact that SO_2 is only observed for the pure sulfonyl azide tells us that though the kinetics as seen by DSC are very similar there are more to the story. A possibility is that the SO_2 producing reaction has a low enthalpy and, therefore, does not contribute significantly to the DSC trace. In addition we do not have a quantitative measure of the amount of SO_2 that is formed. Obviously since there are no hydrocarbons present the nitrenes formed in pure 1,3-BDSA react in other ways than in the polymer. The high enthalpy in the pure state can be explained if the formation of nitrenes is followed by a fast reaction with high enthalpy. Yasuda et al. [20] has theoretically estimated the enthalpy of the coupling reaction in Scheme 7(a) for phenylnitrene to be as large as −362 kJ/mol and E_a to 27.67 kJ/mol. In the pure sulfonyl azide it is likely that nitrenes formed will combine by Scheme 7(a) while it is more unlikely in diluted form. This could account for much of the high reaction enthalpy for pure 1,3-BDSA.

Table 2
Result of DSC kinetic analysis compared with values reported by Breslow et al. [12]

	E_a (kJ/mol)	A (10^{15}/s)	n	k (200 °C) (10^{-4}/s)	k (155 °C) (10^{-4}/s)	$t_{1/2}$ (200 °C) (s)	ΔH[a] (kJ/mol)
1,3-BDSA	147	1.16	1.14	596	11.6	12.2	−248
1,3-BDSA in PE	164	37.7	1.16	286	3.56	25.7	−144
p-Toluenesulfonyl azide in various organic solvents [12]					3.80[b]		−147
1,9-Nonanedisulfonyl azide in various organic solvents [12]							−153

[a] Per mole sulfonyl azide.
[b] In tetradecane.

Table 3
Half-lives and 9 times half-lives of 1,3-BDSA in polyethylene Dow Affinity SQ1503 UE

Temperature (°C)	220	200	180	160
$t_{1/2}$ (s)	4.7	25.7	162	1209
$9t_{1/2}$ (min) (99.8% Conversion)	0.71	3.8	24.3	181

Values calculated from Eqs. (2) and (5) and parameter values from Table 2.

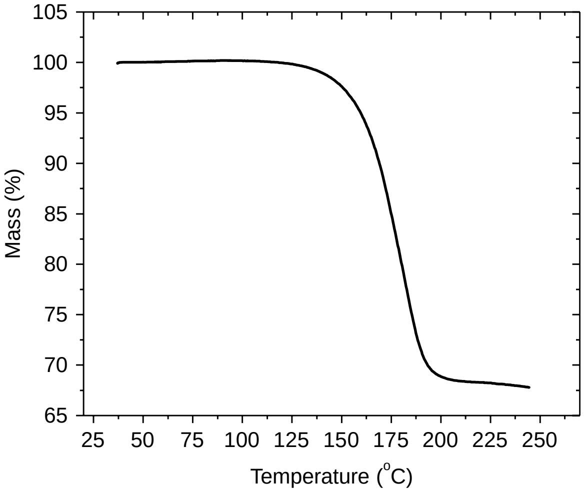


Fig. 6. TGA trace of 1,3-Benzenedisulfonyl azide. Heating rate 20 °C/min.

Many of these details could probably be clarified by further studies, but that is beyond the scope of this work.

Altogether results from the different analyses we have performed gives us evidence that in a stabilized polyolefin blend 1,3-BDSA decomposes to singlet nitrenes that cross-links the polymer by carbon chain insertion. Other reactions such as proton abstraction, loss of the sulfonyl azide group and nitrene coupling are negligible. The good agreement with results from sulfonyl azides in low molecular hydrocarbons suggests that the chain mobility in melted polymers is not an important factor. The concentration and solubility are probably more important.

If we consider the life time (Table 3) of 1,3-BDSA in PE we find that approximately 200 °C is an appropriate processing temperature and it is, therefore, suited for polyolefins. The life time at temperatures below 200 °C is long enough to ensure blending with the polymer in a feeding zone holding for example 160–180 °C.

5. Conclusion

We have studied the thermal decomposition of 1,3-benzenedisulfonyl azide in polyolefins and verified that it leads to polymer chain cross-linking and no degradation. The decomposition follows first order kinetics, and its temperature dependence makes 1,3-BDSA well suited for use at typical polyolefin processing temperatures. In addition 1,3-BDSA is easily dispersed or dissolved in polyolefins at standard mixing conditions. Due to its high reaction enthalpy 1,3-BDSA must be handle with care, but it is easy to prepare from less hazardous chemicals. Transportation and storage can thereby be minimised.

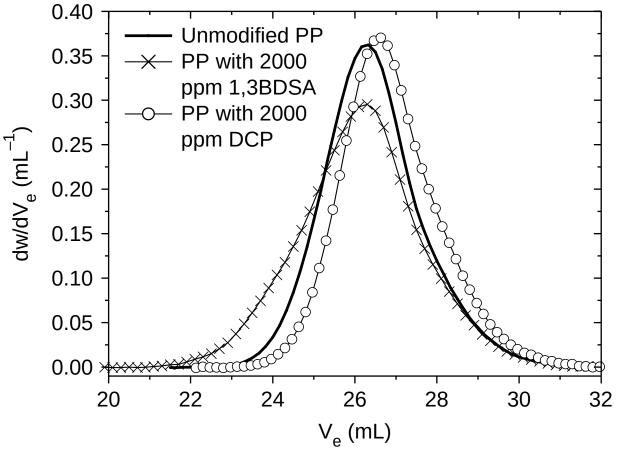


Fig. 7. Normalized SEC concentration chromatograms of unmodified PP and the same PP modified with 1,3-BDSA and dicumyl peroxide. 1,3-BDSA treatment leads to the formation of a high molecular fraction (low V_e), but no formation of low molecular species (high V_e). Opposite to this dicumyl peroxide treatment leads to significant degradation. This indicate that the reactions of 1,3-BDSA do not include macroradicals subjected to chain scission.

We found significant differences between decomposition of pure 1,3-BDSA and 1,3-BDSA in PE. The results for 1,3-BDSA in PE were in accordance with results reported for similar compounds dissolved in low molecular hydrocarbons. Pure 1,3-BDSA decompose faster and in a more complicated manner that we did not fully uncover. If other sulfonyl azides are to be studied for the same purpose, we suggest that they are blended with the actual polymer, or dissolved in a low molecular hydrocarbon if possible.

Due to the absence of degradation in PP processed with 1,3-BDSA, we conclude that the amount of macroradicals formed from proton abstraction by triplet nitrenes are minimal. Nitrenes formed must exist primarily in singlet state and react with the hydrocarbon by insertion.

This paper has considered the reaction kinetics of 1,3-BDSA in polyolefins. SEC results showed that it in fact work as a cross-linker. In two succeeding papers we study in more details properties and molecular structure of PE [9] and PP cross-linked with 1,3-BDSA [10].

Acknowledgements

The authors thank Borealis AS and The Research Council of Norway for financing this work. We also thank Lorenzo Williams, Aud Bouzga and Oddvar Ringstad for assistance with synthesis, NMR and GC-MC, respectively.

References

[1] Breslow DS. Spurlin, US Patent 3203937; 1965.
[2] Terbrueggen RH, Drumright RE. World Patent 2000052091; 2000.
[3] Machado MAL, Kenny JM. Rub Chem Tech 2001;74:198–210.

[4] Benito Gonzalez JL, Ibarra Rueda LM, Gonzalez Hernandez L. Kautschuk Gummi Kunststoffe 1990;43(697):700.

[5] Gonzalez Hernandez L, Rodriguez Diaz A, De Benito Gonzalez JL. Rub Chem Tech 1992;65:869–78.

[6] Borve K, Redford K, Stori A. World Patent 2003020815; 2003.

[7] Borve KL, Redford K, Skattum M. Haavaldsen. World Patent 2001066632; 2001.

[8] Lagendijk RP, Hogt AH, Buijtenhuijs A, Gotsis AD. Polymer 2001;42: 10035–43.

[9] Jørgensen JK, Stori A, Redford K. Polymer 2005, accepted for publication, doi:10.1016/j.polymer.2005.10.084.

[10] Jørgensen JK, Stori A, Redford K. Submitted for publication; 2005.

[11] Curtius T, Meier H. J Prakt Chem 1930;125:358–63.

[12] Breslow DS. Sulfonylnitrenes. In: Lwowski W, editor. Nitrenes. ed. 1. New York: Wiley; 1970 (chapter 8).

[13] Baker DA, East GC, Mukhopadhyay SK. J Appl Polym Sci 2001;79: 1092–100.

[14] Breslow DS, Sloan MF, Newburg NR, Renfrow WB. J Am Chem Soc 1969;91:2273–9.

[15] Reiser A, Leyshon LJ, Johnston L. Trans Faraday Soc 1971;67: 2389–96.

[16] Reiser A, Willets FW, Terry GC, Williams V, Marley R. Trans Faraday Soc 1968;64:3265.

[17] Sbirrazzuoli N, Girault Y, Elegant L. Thermochem Acta 1995;260: 147–64.

[18] Freeman ES, Carrol B. J Phys Chem 1958;394–7.

[19] Denisov ET, Denisova TG, Podikova TS. Handbook of free radical initiators. Floboken: Wiley-Interscience; 2003.

[20] Yasuda N, Yamamoto S, Wada Y, Shozo Y. J Polym Sci, Polym Chem 2001;39:4196–205.