

Contribution to the Modeling of Predepolymerization of Polystyrene

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SYNOPSIS

To optimize the experimental conditions for the recycling of plastic wastes, we modeled the thermal degradation process of a standard polystyrene, having a low polydispersity index. The number of initial ruptures, N_o , in the macromolecular chain during the pyrolysis at 350°C under nitrogen pressure is determined from the gel permeation chromatography results from the experiments with tetralin as the hydrogen donor solvent, assuming that all radicals have been stabilized by this solvent. The calculation shows that there are 23 depropagation reactions, 40 intramolecular transfers, and for n intermolecular transfers, $n - 2$ recombinations, and $N_o - n + 2$ dismutations. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The radical mechanisms during the thermal decomposition of polystyrene have been investigated by many authors.¹⁻⁶ Nevertheless, the agreement between the theoretical and experimental studies is not always evident. This inability to well describe the thermal decomposition mechanisms of thermal rupture of the polymer is mostly due to

- The diversity of the studied polystyrene samples because the method of polymer synthesis has a considerable influence on its structure and therefore on its thermal behavior;⁷⁻⁹
- The diversity of the pyrolysis apparatus (slow heating rate or flash pyrolysis) and the experimental conditions (final temperature, pressure, and nature of the gaseous atmosphere in the reactor)¹⁰; and
- The difficulty of characterizing the composition of the reaction system and the origin of the molecules in the mixture (a huge number of hydrogen transfer reactions possible for a macromolecule).¹¹

To model the global process of thermal degradation, it is necessary to use a standard polystyrene with a polydispersity index close to unity and to study the reactions at a temperature of 350°C where the decomposition rate is low. Such experiments could be performed in microautoclaves fitted with a Pyrex tube specially designed for quantitative analysis of the reaction products. The modeling requires the knowledge of the number of initial scissions and, therefore, the presence of a H-donor solvent is revealed indispensable to know this number. Such studies should permit a better understanding of the depolymerization process. The objective of this study was to optimize the experimental conditions for chemical recycling of plastic waste.

EXPERIMENTAL

Material and Solutions

The standard polystyrene ($I = 1.1$), in powder form is a commercial product, supplied from Interchim Corp. by anionic polymerization ($M_n = 994,000$). Tetralin from Aldrich (98% purity grade) was used without further purification. The polymer solutions were obtained as equimolecular mixtures of styrene units in the polymer chain and tetralin (100 mg of PS and 132 mg of tetralin).

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A design of the microreactor was presented previously.¹² A glass tube (volume $\approx 10 \text{ cm}^3$) was fitted into the body of the reactor to avoid coking of radical products on the steel walls and to enable quantitative analysis of the products. The microautoclave containing the reactants was placed in a fluidized sand bath at 350°C for given period of time, then cooled rapidly and opened after reducing the residual pressure (40 Mpa) to 1 atmosphere. Weight losses in the glass tube were less than 1%.

Analysis of the Products

The mixture of total weight, W_t , was divided into aliquots for NMR, mass spectroscopy, and chromatographic analysis.

Gel Permeation Chromatography

Number-average molecular weights were measured by gel permeation chromatography (KNAUER apparatus) in THF (0.5 mL/min flow), using a differential refractometer, a mixed B column (internal diameter: 7.5 mm; length: 30 cm; pore size: $10 \mu\text{m}$) for heavy products, and a mixed E column (pore size: $3 \mu\text{m}$) for light compounds ($M_n < 30,000$). Calibration of this system was carried out using polystyrene standards. The calibration curve was described by third-order polynomial.

NMR Spectroscopy

^1H -NMR spectroscopy was carried out at 400 MHz on a Bruker AM 400 spectrometer. A known quantity, W_s , of the above mixture was diluted with deuterated chloroform for NMR analysis. The total number of moles, n_i , of each compound i in the solution was calculated from the integrals I_i and I_r of the ^1H signal of compound i and of reference r (hexamethylcyclotrisiloxane, Aldrich 98%) of molecular weight M_r , added to the solution in known quantity (W_r):

$$n_i = \frac{I_i}{H_i} \frac{H_r}{I_r} \frac{W_r}{M_r} \frac{W_t}{W_s}$$

where H_i and H_r are the number of equivalent protons in each signal.

Gas Chromatography/Mass Spectrometry (GC/MS)

The analyses were performed at the Centre de Recherche ELF-ATOCHÉM in Carling, France. The light products ($M < 300$) were analyzed by GC/MS.

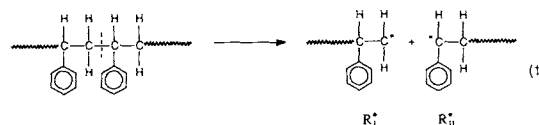
The analyses were carried out on a gas chromatograph equipped with a split/splitless injector and a capillary fused silica column HP1 (length 50 m, internal diameter 0.22 mm) coupled with a quadrupole mass spectrometer NERMAG R 1010C (electron impact ionization 70 eV; source temperature 235°C).

RESULTS AND DISCUSSION

Without H-donor Solvent

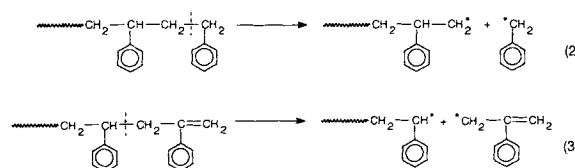
The GPC chromatograms of the degraded polystyrene samples present the same characteristics and contain three well-distinct areas whatever the time of reaction is (Fig. 1). The first peak spreads over 8–10 min of elution time and represents the non-degraded and (or) partially degraded polystyrene with a relatively high molecular weight. The next one is a broad peak representing the oligomers (notably the di-, tri-, and tetramers) and the last one represents the light compounds, mostly styrene.

The results (Table I) show an abrupt drop of molecular weight during the first 20 min of reaction. During this time, a small quantity of light compounds is observed. This initial drop is caused mainly by random scissions in the chain^{13–16} [reaction (1)]:



where R_1^* is a primary macroradical and R_2^* is a secondary macroradical.

In the case of a polystyrene prepared by anionic polymerization (the chain structure of these polymers is more regular than is a free-radical polymerization polystyrene), it was shown that additional chain-end initiation could also occur^{17,18} [reactions (2) and (3)]:



However, the important drop of the molecular weight as well as the absence of light products when using tetralin as solvent (cf. next paragraph) show that at 350°C reactions (2) and (3) are certainly negligible with respect to reaction (1).⁹

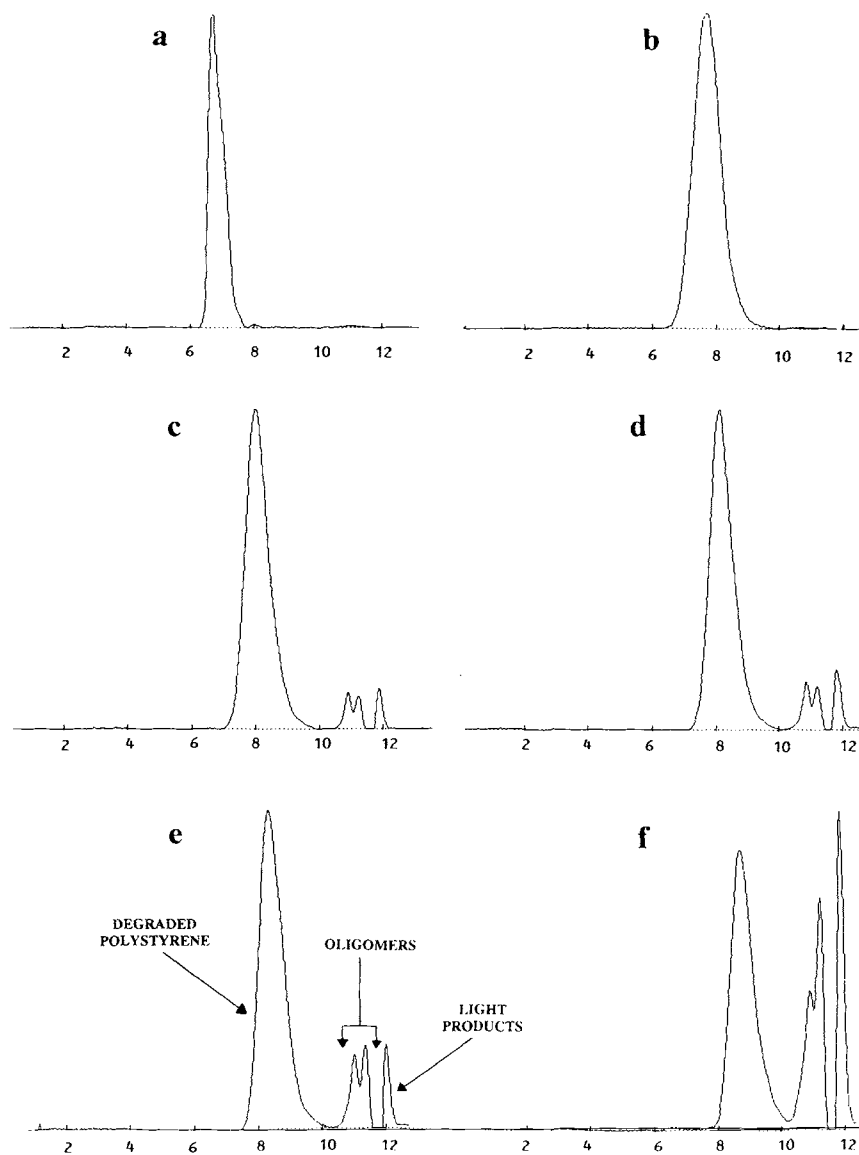


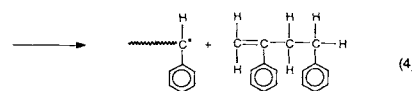
Figure 1 GPC curves (mL/min) obtained from the pyrolysis of polystyrene without tetralin: (a) initial polystyrene and (b) after 20 min, (c) 40 min, (d) 60 min, (e) 80 min, and (f) 150 min of pyrolysis time.

When the time of thermal treatment increases, the drop becomes gradual. After 150 min, the percentage of partially degraded polystyrene represents about half of the initial polymer. Its molecular weight tends to an asymptote,^{7,19} where $M_n \approx 13,000$. The reaction medium is then the place of numerous reactions:

- On the one hand, some intramolecular transfer reactions notably from hydrogen atoms situated on the tertiary carbons which are the most labile. For example, the transfer of a hydrogen in position 3 with regard to the active center of the radical R_{II}^{\bullet} leads to a new radical:



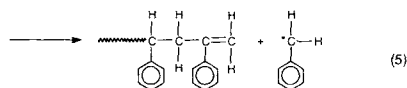
This radical can break in the β position either on the left with formation of an other radical and a dimer:



or on the right with formation of an olefin and a benzyl radical:

Table I GPC Results of Thermal Decomposition at 350°C of the Standard Polystyrene Without Tetralin

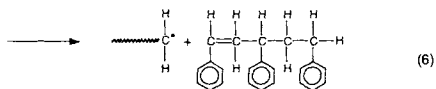
Time (min)		Degraded Polystyrene	Trimers and More	Dimers	Light Products (Styrene)
0	M_n	994,518			
	% Aera	100	0	0	0
	I	1.10			
20	M_n	125,290	365	208	104
	% Aera	98.62	0.7	0.43	0.24
	I	2.08	1.05	1.02	1.00
40	M_n	58,326	365	208	104
	% Aera	91.95	3.00	2.32	2.73
	I	2.02	1.05	1.03	1.01
60	M_n	47,143	365	208	104
	% Aera	88.48	3.98	3.13	4.42
	I	1.81	1.07	1.03	1.02
80	M_n	29,635	360	212	106
	% Aera	83.6	5.91	5.56	4.93
	I	1.76	1.08	1.02	1.01
150	M_n	12,920	370	204	110
	% Aera	55.05	18.52	11.54	14.90
	I	1.71	1.06	1.01	1.01



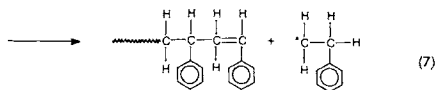
However, mechanism (4) should be predominant because a secondary radical is more stable than is a primary one. Similarly, the transfer of a hydrogen atom in position 4



leads to the formation of a dimer and a new radical R_{II}^* if there is a β -scission on the left:



or to the formation of an olefin and the $\varphi\text{CH}_2\text{CH}_2$ radical, if the β -scission is on the right:



Trimers and tetramers can be formed according to analogous reactions, but the heaviest oligomers

are not detected in the GPC curves, so we can conclude that the intramolecular hydrogen transfers become negligible when the hydrogen is too far away from the active center (on a carbon situated in a position further than 7). The NMR spectra of the pyrolysis products after 80 min of the reaction show that toluene is present in a very small quantity (traces), whereas ethylbenzene, cumene, and α -methylstyrene are missing. These results are in good agreement to those found by Chien and Kiang²⁰ and Cascaval et al.²¹ at the same temperature. The GC-MS analysis of the oligomer fraction (at 150 min reaction time) shows that the dimers consist of 45% of diphenyl-2,4-butene-1 ($M_n = 208$) coming from reaction (4). Other olefins, such as diphenyl-1,3-propene-1 ($M_n = 194$) and diphenyl-2,4-pentene-1 ($M_n = 222$), are also present in small amounts (respectively, 2 and 3%). We also found 1,3-diphenylpropane (33%), which is coming from an intramolecular transfer of a hydrogen atom in position 5 from a secondary radical followed by a right β -scission. Formation of diphenylbutane (11%) is due to the same mechanism, but the intramolecular transfer is provided from a hydrogen atom in position 6 from a primary radical. These products could also be formed by recombination of the radicals $\varphi\text{CH}_2\text{CH}_2$ and φCH_2 . The other compounds are in negligible quantity. As for trimers, the chief com-

ponents are triphenyl-1,3,5-hexene-1 ($M_n = 312$) and triphenyl-1,3,5-pentane ($M_n = 300$)¹¹ derived, respectively, from a hydrogen transfer in position 5 of a primary radical and in position 7 of a secondary radical:

- On the other hand, some depropagation reactions: By rupture in the β position of radicals, the amount of styrene formed could be determined either by GPC (if the other light compounds like toluene, ethylbenzene, etc., are not present¹⁹ or by NMR (peaks at 5.2 and 5.6 ppm). The olefinic protons of the oligomers are also observable in this region. The quantity of styrene found by means of these two techniques after 80 and 150 min of the reaction are practically identical.
- Finally, some intermolecular transfer reactions: The radicals R_I^{\cdot} or R_{II}^{\cdot} reacting with hydrogens of other chains. If the reaction takes place near the chain end, the mechanisms are similar to those described previously. When the transfer occurs on a carbon distant from the chain end, and if it is followed by a β -scission either on the left or on the right, there is a formation of a secondary radical and a high molecular weight olefinic compound:



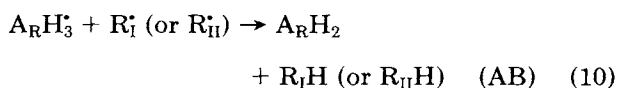
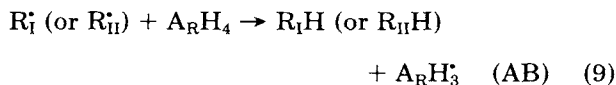
In Presence of Solvent

The H-donor solvents were frequently used in a coal hydroliquefaction process to stabilize the radicals produced during the rupture of the lateral chains linking the polyaromatic entities.^{22,23} To model this process, we have already studied the reactions between a model radical precursor, benzyl phenyl ether (BPE), and different hydroaromatics solvents (noted A_RH_2) such as tetralin at 350°C. It was shown that the stabilization of the radicals could occur in three different ways:

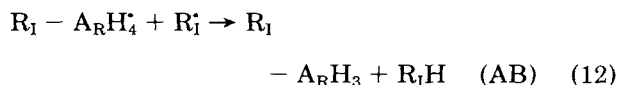
- By recombination of the benzyl and phenoxy radicals inside the radical cage, with formation of *o*- and *p*-benzylphenols. In our case of thermal decomposition of polystyrene, this type of mechanism is unlikely and it would not change the molecular weight of the polymer.
- For a very small part, by the methylenic hydrogens of the nondegraded BPE, leading to the formation of benzaldehyde. This mecha-

nism is equivalent to the mechanisms of intermolecular transfers previously described. However, in the case of polystyrene, the absence of heteroatom makes the hydrogens less labile than those of BPE.

- Mainly by the solvent: It was shown that 85% of the benzyl and phenoxy radicals were stabilized by the hydroaromatic hydrogens of tetralin. In the case of polystyrene, the radicals R_I^{\cdot} and R_{II}^{\cdot} will be preferentially stabilized by the two abstraction processes (AB):



where A_RH_2 is the aromatic counterpart of the solvent, i.e., 1,2-dihydronaphthalene (and then naphthalene A_R with two supplementary abstractions). These compounds are, however, not detected in ¹H-NMR because the radicals formed are in too small an amount at 350°C. Some secondary reactions can also occur, the main one being the addition of the radical R_I^{\cdot} on the solvent:



In mechanism (12), the radical R_I^{\cdot} was stabilized by an addition process and the compound obtained, $R_I A_RH$, has a molar mass very close to the mass of the stabilized radical.

The results of the experiments with tetralin as a solvent (Table II) show that the molecular weight always drops abruptly in the beginning of the reaction but are still more important than are those obtained without solvent. No oligomer or light product is observable until 40 min of reaction time.¹⁰ One can therefore reasonably think that until this time practically all the radicals were stabilized by tetralin according to reactions (9)–(12). The presence of traces of styrene or oligomers would not change anyway the molecular weight since these products appear only for a reaction time longer than 40 min. The chromatograms seem to indicate that these oligomers are principally dimers, which proves that intramolecular mechanisms are now limited to hydrogen linked to carbons close to the active center (on position 2 or 3). The transfer mechanisms from

Table II GPC Results of Thermal Decomposition at 350°C of the Standard Polystyrene with Tetralin^a

Time (min)		Degraded Polystyrene	Dimers
0	M_n	994,518	
	% Aera	100	0
	I	1.10	
20	M_n	169,282	0
	% Aera	100	0
	I	2.25	1.05
40	M_n	144,077	208
	% Aera	99.9	0.1
	I	2.08	1.05
60	M_n	66,115	208
	% Aera	96.82	3.18
	I	2.05	1.07
80	M_n	63,128	208
	% Aera	96.42	3.58
	I	2.02	1.08
150	M_n	52,050	208
	% Aera	82.80	17.20
	I	1.87	1.05

The low quantity of light products, located in the solvent peak, is not measured.

hydrogen atoms situated on the distant carbons are now insignificant because there are in competition with those of the H-donor solvent.

Modeling of the Predepolymerization Mechanisms

If we want to model the mechanisms of pre-depolymerization, it is necessary to determine the number of initial ruptures N_o according to

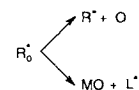
$$P \rightarrow (N_o + 1)R_o^*$$

where R_o^* represents a macroradical (or a biradical) as the ruptures are not supposed to be produced at the chain ends. The number of macromolecules, M_o , is determined by the ratio r between the mole number of partially degraded polystyrene, calculated from molecular weight (Table I) and the mol number of initial polymer. The calculation is based on the experiments with tetralin because we will consider that the number of the radicals formed is sufficiently low and therefore they are practically all stabilized by the solvent. For 20 min of the reaction time, r

= 5.87; it means that there are about six times more macromolecules than initially—so $M_o = R_o^* = 6$ and $N_o = 5$.

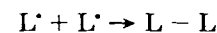
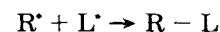
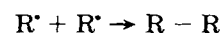
To precise these results, further experiments will be done by varying the concentration and the nature of the H-donor solvent. Without solvent, although the kinetic of decomposition could depend on the medium viscosity, it can be considered that the number of initial ruptures N_o at a given time is the same as that obtained with tetralin. As we seen above, the macroradicals R_o^* can be stabilized:

- (i) By intramolecular transfer according, e.g., to mechanisms (4) and (5), as follows:



where R^* is a macroradical; L^* , a “light” radical (such as ϕCH_2^*); O , an oligomer; and MO , a macroolefinic compound. If we exclude for the moment all ulterior intermolecular transfer, the radicals would undergo some termination reactions:

- either by recombination: In this case, there are three possibilities—



In this view, the number of obtained macromolecules of $R - R$ and $R - L$ type decreases by one unity due to recombination, with regard to the number of initial radicals R_o^* . These macromolecules will be situated in the first GPC peak representing the partially degraded polystyrene and it excludes the presence of the $L - L$ -type compounds which are situated in the oligomer area in the GPC curves.

- Or by dismutation: A macroradical (now noted HR^*) permits its hydrogen to stabilize another radical R^* with formation of a macroolefinic compound:



and in this case, the number of macromolecules is equal to R_o^* . Consequently, it is not possible to obtain a number of mac-

romolecules superior to the number of initial radicals by intramolecular transfers only. The same is true for the depropagation processes.

- (ii) By intermolecular transfer: If the hydrogen atom is linked to a chain-end carbon, we are brought back to the previous case. However, these carbons are in very low proportion in comparison to those situated in the middle of the chain ($\sim 15/19,000$); therefore, we suppose that oligomers can be formed only via intramolecular reactions. If the transfer takes place according to mechanism (8), we obtain by recombination the same number of macromolecules as initial radicals but this number increases by one unity for every dismutation. We arrive at the same conclusion if the transfer is accomplished via the radicals R^{\cdot} or L^{\cdot} .

These observations permit us to describe the whole degradation process. In the experiments with tetralin, we have seen that the number of initial macromolecules was about 6. In Figure 2(a), we present an example of macromolecular chain ruptures, with calculated values of M_n , M_w , and I (166,000, 378,000, and 2.28, respectively) being close to the experimental data (169,000, 380,000, and 2.25; cf. Table II). There are, of course, several possibilities, but to obtain a polydispersity index value $I = 2.25$, it is necessary that the macroradicals formed during the thermal treatment have very different lengths.

Without solvent and for 20 min of reaction time [Fig. 2(b)], we can determine the number of depropagation and intramolecular transfer reactions calculated from the ratios r' , r'' , and r''' . The ratio r' , representing the number of styrene molecules on the number of initial molecules, shows that there are 23 molecules of monomer per one chain and, therefore, 23 depropagation reactions. The other ratios r'' and r''' are defined to calculate the number of molecules of dimers and trimers and more, taking, respectively, a mass of 208 and 365 on the GPC curve. We found 21 dimers and 19 trimers formed for a macromolecular chain. It means that there are 40 intramolecular processes. In reality, this number of intramolecular reactions is certainly overestimated because the corresponding areas on the GPC chromatograms contain few recombination products of the L—L type.

The results obtained for the partially degraded polystyrene show that after 20 min of the reaction the ratio r is now equal to 7.98. Therefore, there are

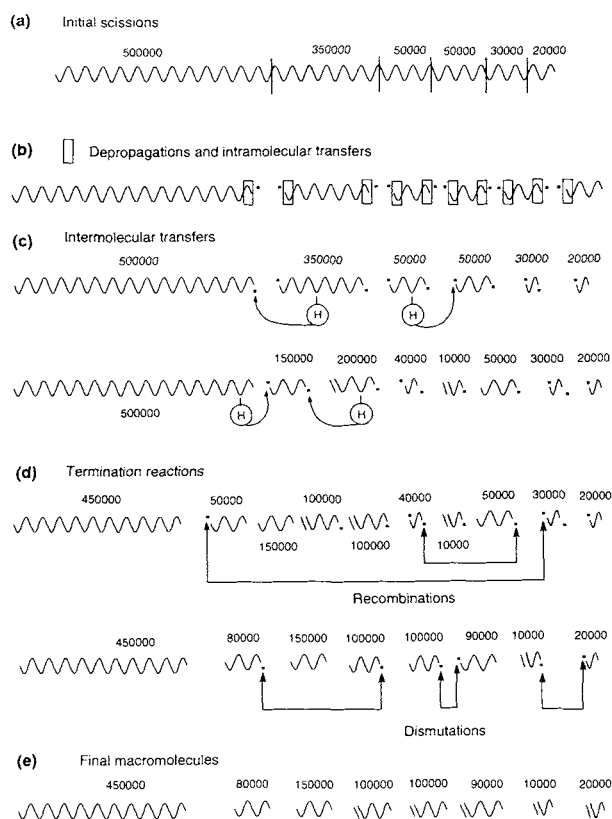


Figure 2 Modeling of the thermal decomposition of the standard polystyrene.

two additional macromolecules for each chain, stemming evidently from intermolecular reactions followed by dismutations, as we have seen above. It is not possible for the moment to evaluate the number of intermolecular transfers n , but to obtain two supplementary macromolecules, it is necessary to consider $n - 2$ recombinations and $N_0 - n + 2$ dismutations. In Figure 2(c), we present an example for $n = 4$ chosen arbitrarily. According to the previous formulas, the number of recombination and dismutation reactions has to be 2 and 3, respectively, to obtain the final number of macromolecules equal to 8 [Fig. 2(d)], with M_n , M_w , and I values of 125,000, 260,000, and 2.08, being in agreement with the experimental data (124,000, 259,000, and 2.08, respectively; cf. Table II).

CONCLUSION

This work shows that it is possible to give a representative picture of the radical mechanisms during the process of pre-depolymerization of polystyrene utilizing a standard polymer with a low polydispersity.

sity index. To improve the model, the number of initial scissions could be determined using other H-donor solvents more effective than is tetralin, as, e.g., 9,10-dihydrophenanthrene or anthracene. Such a modeling can therefore help to a better understanding of the parameters influencing the thermal degradation of the polymer (synthesis conditions, polydispersity, polymer properties, chain length, etc.) and seems to be useful for description of degradation process in the presence of a catalyst.

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