Macromolecules

Volume 35, Number 9 April 23, 2002

Communications to the Editor

Efficient Control on Molecular Weight in the Synthesis of Poly(*p*-xylylene)s via Gilch Polymerization

Friedel Brink-Spalink and Andreas Greiner*

Philipps-Universität Marburg, FB Chemie,
Institut für Physikalische Chemie, Kernchemie,
Makromolekulare Chemie und Wissenschaftliches Zentrum
für Materialwissenschaften, Hans-Meerwein-Str.,
D-35032 Marburg, Germany

Received April 9, 2001
Revised Manuscript Received February 14, 2002

Introduction. Poly(*p*-xylylene)s (PPX) are of interest for technical applications and for academic research due to their interesting property profile and their numerous useful technical applications.[1] PPX can be synthesized by a variety of synthetic routes, which have been discussed extensively in several reviews.[1,2] The synthesis of PPXs is usually accomplished by polyreaction of 1,4-quinodimethanes although the routes for generating 1,4-quinodimethanes can be very different. The formation of 1,4-quinodimethanes from [2.2]paracyclophanes by vapor phase pyrolysis, the so-called Gorham-route,[3] has received technical significance whereas the generation of 1,4-quinodimethanes by base-induced dehydrohalogenation of 4-halogenomethyltoluenes, the so-called Gilch-route,[4] became a standard laboratory procedure in particular for nonvolatile or temperature-sensitive starting materials.

High molecular weight PPX derivatives can be accomplished by the Gilch route with 4-halomethyltoluenes,[5,6] but the efficient control of molecular weight is still an unsolved problem. A molecular weight control has been reported for Gilch-type polymerizations with 1,4-bis(chloromethyl)benzenes in the presence of 4-*tert*-butylbenzyl chloride.[7] Since a radical chain growth mechanism is anticipated for the polymerization of corresponding 1,4-quinodimethanes formed upon base-induced 1,6-dehydrohalogenation reaction of 4-halomethyltoluenes, several retarders for radical polymerizations were tested for control of the chain growth for the synthesis of poly(2(or 3)-phenylethyl-*p*-xylylene) (**2**) by the Gilch polymerization starting from 2-methyl-5-chloromethylbibenzyl (**1**).[8]

This paper reports on a new efficient method for the control of molecular weights of PPXs prepared the Gilch route by addition of triethylamine.

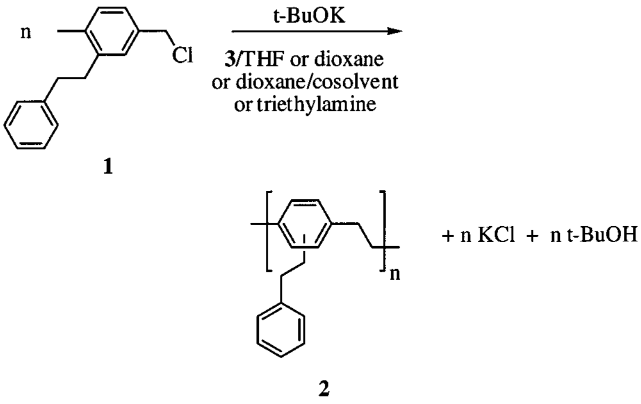
Experimental Part. a. Materials. Compound **1** was prepared following a previously published procedure.[5] Triethylamine, dioxane, cyclohexane, and *n*-hexane

Table 1. Yield and M_n of 2 Obtained by Gilch Polymerization in Pure Dioxane or in a Mixture of Dioxane and a Cosolvent (*n*-Hexane, Cyclohexane, or Triethylamine)

entry	cosolvent	amount [vol %]	yield of 2^a [%]	M_n	M_w
1			48	232 000	601 000
2	*n*-hexane	50	15	105 000	220 000
3	cyclohexane	50	51	149 000	411 000
4	triethylamine	12	58	77 000	152 000
5	triethylamine	25	34	19 000	53 000
6	triethylamine	50	59	31 000	48 000
7	triethylamine	75	51	12 000	21 000
8	triethylamine	88	42	5 600	9 600
9	triethylamine	100	3	2 900	3 500

[a] Yield of **2** is given relative to the molar amount of **1** (5 mmol).

Scheme 1



10.1021/ma010623c CCC: $22.00 © 2002 American Chemical Society
Published on Web 03/29/2002

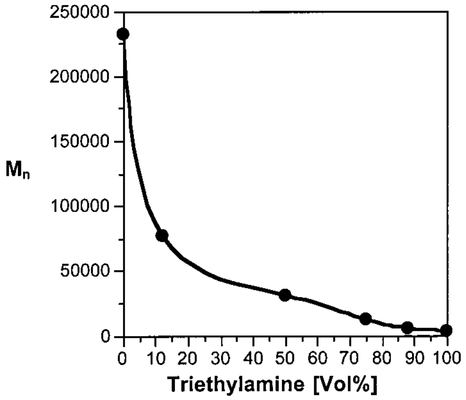


Figure 1. Molecular weight (M_n) of **2** as a function of the amount (vol %) of triethylamine relative to dioxane.

were dried under an argon atmosphere using standard techniques. Potassium *tert*-butoxide (*t*-BuOK) and 4-methoxybenzyl chloride (**3**) were used as received (Aldrich). All reactions were carried out under an argon atmosphere.

b. Measurements. ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded on Bruker AC 300 in $CDCl_3$. GPC was performed with THF as solvent and a set of 5 μm (pore size) mixed bead columns (PSS) and a Viscotek detector applying universal calibration. It should be noted here that the determination of absolute molecular weight by static light scattering can result in deviations of molecular weight due to aggregation.[5,9] To resolve the problem of aggregation, molecular weights were obtained by GPC using universal calibration (aggregates are unstable in shear fields).

c. Synthesis of 2 in the Presence of 3. A 250 mL flask was charged with 1.12 g (10 mmol) of *t*-BuOK and 40 mL of THF as solvent. This mixture was heated to reflux. 2.00 g (5 mmol) of **1** and 0.1 or 10 mol % (related to **1**) of **3** were dissolved in 10 mL of THF and were rapidly added by syringe. This mixture was heated to reflux for 2 h. The reaction was quenched by addition of the hot reaction mixture to 500 mL of methanol. **2** was isolated by filtration, drying in a vacuum, reprecipitation from chloroform/methanol, and finally drying in a vacuum. For yields and molecular weight see Table 1.

d. Synthesis of 2 with Different Solvents. The polymerizations were performed as described above, but THF was replaced by solvents as given in Table 1 without **3**. For yields and molecular weights see Table 1.

Results and Discussion. For comparability we have used the same system as reported previously with respect to starting material, synthetic route, and resulting polymer.[8] **1** was reacted with *t*-BuOK to give **2** in the presence of **3** in THF, in dioxane, in dioxane and a cosolvent, or in triethylamine (Scheme 1).

To begin with we have investigated the control of M_n of **2** by polymerization in the presence of 4-methoxybenzyl chloride (**3**) with THF as solvent. However, neither 0.1 mol % (M_n = 483 000) nor 10 mol % (M_n = 173 000) of **3** resulted in efficient control of M_n in comparison to the control experiment without any **3** (M_n = 134 000).

Next we have investigated the control of M_n of **2** by variation of the solvent system. Our concept was to induce precipitation of **2** by polymerization in a poor solvent for **2** and consequently limit chain growth. M_n of **2** amounted to 232 000 with dioxane as solvent but dropped significantly with 1:1 mixtures *n*-hexane/dioxane (M_n = 105 000) and cyclohexane/dioxane (M_n = 149 000) (Table 1). However, most significant reduction of M_n was found for reactions in triethylamine/dioxane (M_n = 49 000). Systematic variation of triethylamine concentration showed drastic decrease of M_n with increasing concentration of triethylamine (Figure 1). Polymerization in triethylamine without dioxane resulted in **2** with remarkably low M_n = 2900. It is obvious that full control on molecular weight can be accomplished in the Gilch polymerization starting from **1** simply by addition of triethylamine.

^{1}H and ^{13}C NMR spectroscopies showed that polymer chains are terminated by triethylamine moieties. The signals at 2.24−2.14 ppm in the ^{1}H NMR spectrum (Figure 2) were assigned to the two methylene protons

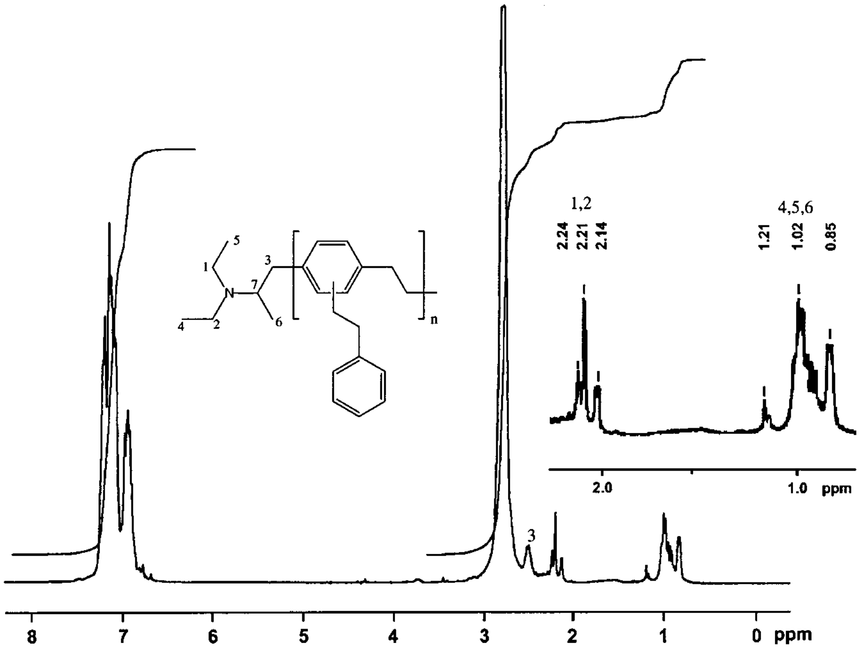


Figure 2. ^{1}H NMR spectrum of **2** (Table 1, entry 9).

of triethylamine end group (1, 2) and the signal at 2.55 to the benzylic protons (3). The signals at 1.21−0.85 ppm can be assigned to the protons of the methyl groups of the triethylamine end groups (4, 5, 6). The signal of the protons of the methine groups (7) are expected in the ^{1}H NMR spectrum at 3.18 ppm. However, the methine protons have not been observed here, most likely due to their poor relative intensity. The integrals for the triethylamine end groups in the ^{1}H NMR spectrum in conjunction with M_n obtained by GPC result in end-group functionalities of <2. $M_n = 1800$ g/mol was calculated from the ^{1}H NMR spectrum (Figure 2) on the basis of **2** with two triethylamine end groups. However, $M_n = 3100$ g/mol is calculated on the basis of one triethylamine end group, which is closer to the results of the GPC analysis (Table 1, entry 9).

It is obvious that termination of the chain growth takes place by triethylamine through chain-transfer reaction combined with a significant decrease in molecular weight. Triethylamine has been successfully used as chain-transfer agent in the radical polymerization of styrene[10] and in the oxidative polymerization of 2,6-dimethylphenol.[11] It is also noteworthy that Gilch polymerizations in the presence of water, CO_2, and 1,1-dipenhylethene did not result in any effect of molecular weight of **2**. No systematic variation was found for chlorine content of **2** (by elemental analysis) and molecular weight of **2**. These findings and the fact that benzyl chlorides (here compound **3**) do not effect chain growth favor a radical 1,6 polymerization via corresponding 1,4-quinodimethanes originating from 4-halomethyltoluenes. However, an anionic mechanism still cannot be ruled out completely on the basis of these data. Indeed, the mechanism might be different for 4-halomethylbenzenes and for 1,4-bis(halomethyl)benzenes. Future work will focus on further investigation of chain growth mechanism for PPXs and exploitation of potential for new PPXs design by control of molecular weights and end groups.

Acknowledgment. The authors are indebted to Deutsche Forschungsgemeinschaft for financial support.

References and Notes

(1) Beach, W. F.; Lee, C.; Bassett, D. R.; Austin, T. M.; Olson, R. *Encyclopedia of Polymer Science and Technology*; Wiley & Sons: New York, 1989; Vol. 17, p 990.

(2) Greiner, A.; Mang, S.; Schäfer, O.; Simon, P. *Acta Polym.* **1997**, *48*, 1.

(3) Gorham, W. F. *J. Polym. Sci., Part A-1* **1966**, *4*, 3027.

(4) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci., Part A-1* **1966**, *4*, 1337.

(5) Schäfer, O.; Greiner, A.; Antonietti, M.; Zisenis, M. *Acta Polym.* **1996**, *47*, 386.

(6) Schäfer, O.; Brink-Spalink, F.; Smarsly, B.; Schmidt, C.; Wendorff, J. H.; Witt, C.; Kissel, T.; Greiner, A. *Macromol. Chem. Phys.* **1999**, *200*, 1942.

(7) Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094.

(8) Schäfer, O.; Brink-Spalink, F.; Greiner, A. *Macromol. Rapid Commun.* **1999**, *20*, 190.

(9) Schnabbelegger, H.; Antonietti, M.; Göltner, C.; Stapff, I. H.; Brink-Spalink, F.; Greiner, A. *Acta Polym.* **1999**, *50*, 391.

(10) Moad, G.; Solomon, D. H. In *The Chemistry of Free Radical Polymerization*; Elsevier: New York, 1995; p 245.

(11) Hay, A. S., personal communication.

MA010623C