

Slow initiation by *tert*-butoxybenzenes in living cationic polymerization of isobutylene

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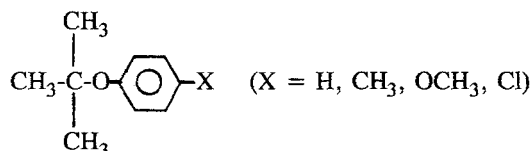
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SUMMARY

tert-Butoxybenzenes including the 4-substituted derivatives of anisole, toluene and *p*-chlorobenzene have been synthesized and studied as initiators in combination with TiCl_4 for polymerization of isobutylene (IB) in CH_2Cl_2 /methylcyclohexane (MeCHx) solvent mixtures at -78°C . Living polymerizations with slow initiation were observed by the all-monomer-in (AMI) and incremental monomer addition (IMA) techniques, and polymers with narrow molecular weight distribution (MWD) ($M_w/M_n < 1.1$) were obtained under certain conditions. Aging of the initiating system prior to charging the monomer does not improve the initiating efficiency. It has been found that the initiating efficiency can be increased by increasing the solvent polarity, however, the relative volume of CH_2Cl_2 is limited in order to avoid polymer precipitation and bimodal MWD.

INTRODUCTION

There has been significant developments in the field of living cationic polymerization of olefins during the past few years (see Refs. 1-4 for recent reviews). Since the discovery of living carbocationic polymerization of isobutylene by initiation with *tert*-ester^(5,6) and *tert*-ether derivatives⁽⁷⁾, a large number of different initiators of these types have been investigated in connection with BCl_3 and TiCl_4 coinitiators⁽¹⁻⁴⁾. In the reported instances of *tert*-ether initiators, cumyl and aliphatic methyl ethers were used to induce living polymerization of IB. Aliphatic *tert*-esters^(6,8) and *tert*-ethers⁽⁸⁾ have been found to yield low initiating efficiencies. To our knowledge it has not been previously investigated whether it is possible to mediate living polymerization of IB by *tert*-phenoxides. This paper concerns the following *tert*-butoxybenzene derivatives as initiators for living carbocationic polymerization of IB:



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EXPERIMENTAL

A. Materials

CH_2Cl_2 (Bie & Berntsen) was refluxed over CaH_2 for 24 hours before distillation, then Et_3Al was added and it was distilled before use. Methylcyclohexane (MeCHx) (Aldrich) was refluxed with cc. H_2SO_4 for 12 hours, washed to neutral with water, dried with MgSO_4 , and distilled from CaH_2 prior to use. TiCl_4 (Aldrich) was distilled from CaH_2 under dry nitrogen atmosphere. Trifluoromethanesulfonic acid, 4-methoxyphenol, phenol, p-cresol, 4-chlorophenol, triethylamine and 2,6-di-*tert*-butylpyridine (DtBP) (all from Aldrich) were used as received. Isobutylene (Hydro Gas Danmark) was passed through a column filled with barium oxide and molecular sieves before condensation.

B. Synthesis of initiators

The *tert*-butoxybenzene derivatives were synthesized according to a published procedure for 4-*tert*-butoxyanisole⁽⁹⁾. 90 mmol of selected phenol derivative (4-methoxyphenol, phenol, p-cresol or 4-chlorophenol) was dissolved in 90 ml dichloromethane together with 70 ml (900 mmol) isobutylene at -78°C followed by the addition of 7 mmol (630 μl) trifluoromethanesulfonic acid. After stirring for 4 hours at -78°C , 7 mmol triethylamine was charged, and then the reaction mixture was allowed to warm to room temperature. The volatiles were removed by rotary evaporation and the residue was extracted with 350 ml hexanes, washed with 0.1M NaOH solution and concentrated by rotary evaporation. Purification was carried out by column chromatography on Merck Silica Gel 60 using dichloromethane/hexanes (1:2) as eluent, and a final gradient eluent by steadily increasing the dichloromethane content starting with pure hexanes. The isolated products were essentially pure compounds as analyzed by TLC and ^1H NMR, which gave the following results: 4-*tert*-butoxyanisole: $\delta = 1.30$ ppm singlet (9H), 3.80 ppm singlet (3H), 4.78 ppm doublet (2H), 4.83 ppm doublet (2H); *tert*-butoxybenzene: $\delta = 1.35$ ppm singlet (9H), 7.0-7.4 ppm multiplet (5H); 4-*tert*-butoxytoluene: $\delta = 1.32$ ppm singlet (9H), 2.32 ppm singlet (3H), 6.89 ppm and 7.08 ppm, doublets (each 2H); 4-*tert*-butoxychlorobenzene: $\delta = 1.32$ ppm singlet (9H), 6.92 doublet (2H), 7.20 ppm doublet (2H). Yields were $\sim 70\%$ by these syntheses.

C. Polymerizations

All polymerizations were carried out using conventional laboratory techniques with rubber capped glassware under dry nitrogen atmosphere, and performing all transfers through transfer needles or by syringes as previously described⁽¹⁰⁾.

D. Characterizations

^1H NMR measurements were carried out in CDCl_3 with TMS as internal standard on a Bruker AC-250 instrument. GPC analyses were made by two different instruments. In case of molecular weights $< 50,000$ a Waters Model 510 with Nucleosil columns of 250x8mm, 500 \AA -5 μm and 100 \AA -3 μm and Daisogel 250x8mm, 200 \AA -5 μm . For MWD determination of samples with molecular weights $> 50,000$ a GPC equipment consisting of a Knauer pump FR-30 and Knauer differential refractometer equipped with the column combination of 500x8mm Shodex A-805, 600x7.5mm TSK G4000 and 600x7.5mm TSK G3000. Calibrations were made by narrow MWD polystyrenes (PSt) and calculations of molecular weights were based on a previously determined relationship between polyisobutylene (PIB) and polystyrene calibration curves obtained by calibrations with narrow MWD PIB and PSt standards.

RESULTS AND DISCUSSION

Orienting polymerization experiments were carried by the AMI technique^(6,13). In Figures 1-3, the M_n and the ratio between the number of polymer molecules (N) formed and initiator molecules (I_0) (N/I_0 ; in the inset) are plotted as a function of the weight of polymer (W_p) using 4-*tert*-butoxyanisole, 4-*tert*-butoxybenzene, and 4-*tert*-butoxytoluene initiators, respectively. In the case of 4-*tert*-butoxychlorobenzene somewhat erratic results were obtained and therefore further studies were not made with this compound. As shown in Figures 1-3, M_n increases with W_p but it is significantly higher than theoretical values (obtained by assuming living polymerization with 100 % initiating efficiency). As the M_w/M_n values indicate polymers with relatively narrow MWDs were obtained ($M_w/M_n = 1.13 - 1.29$). As the insets in these Figures exhibit the number of chains (N) is smaller than I_0 and it increases with W_p . In the absence of chain transfer and permanent termination such behavior is typical for living polymerization with slow initiation^(11,12,14,15).

Further experiments have been carried out using the IMA technique to test the effect of aging for the 4-*tert*-butoxytoluene/ $TiCl_4$ initiating system in the presence of *DtBP*. Figure 4 shows the results of two sets of experiments. In one of the IMA series the initiation of polymerization occurred without aging whereas 30 minutes aging of the initiating components was applied before charging IB in the other experiment. As shown clearly in the inset in Figure 4, aging does not have any significant effect on the rate of initiation, i. e. the N/I_0 versus W_p plots are the same in the absence and in the presence of aging of the initiating system.

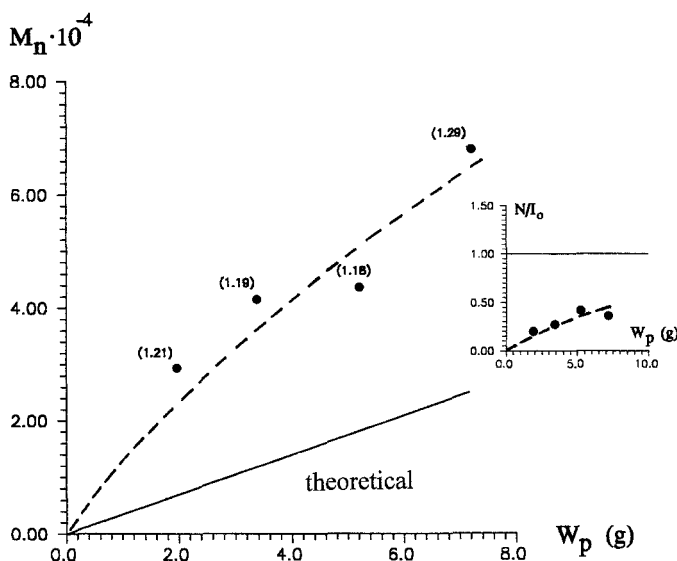


Figure 1. M_n and N/I_0 (inset) versus W_p plots obtained by the AMI technique for the 4-*tert*-butoxyanisole/ $TiCl_4$ /IB/*DtBP*/ CH_2Cl_2 :MeCH_x 40/60 v/v/-78 °C polymerization system. $[I]_0 = 2.9$ mM, $[TiCl_4] = 45$ mM, $[DtBP] = 2.9$ mM; total volume = 99, 101, 103 and 105 ml corresponding to 4, 6, 8 and 10 ml IB added. Numbers in parentheses indicate M_w/M_n values.

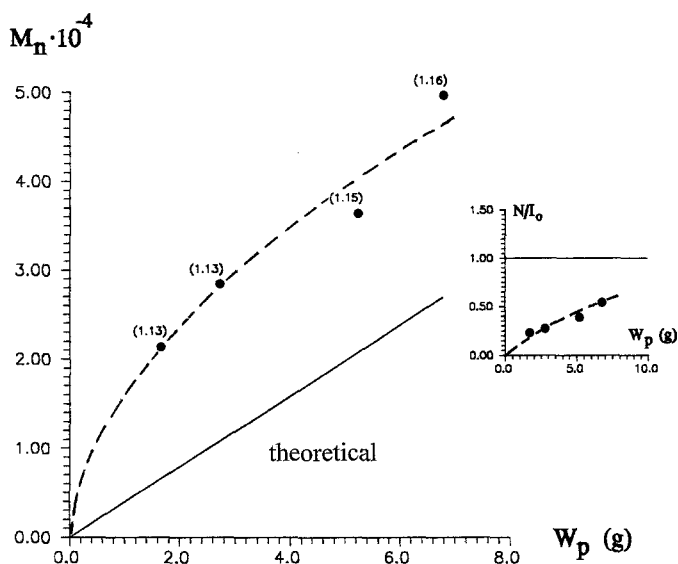


Figure 2. M_n and N/I_0 (inset) versus W_p plots obtained by the AMI technique for the 4-*tert*-butoxybenzene/ $TiCl_4$ /IB/*DtBP*/ CH_2Cl_2 :MeCHx 40/60 v/v/-78 °C polymerization system. $[I]_0 = 2.9$ mM, $[TiCl_4] = 45$ mM, $[DtBP] = 2.9$ mM; total volume = 99, 101, 103 and 105 ml corresponding to 4, 6, 8 and 10 ml IB added. Numbers in parentheses indicate M_w/M_n values.

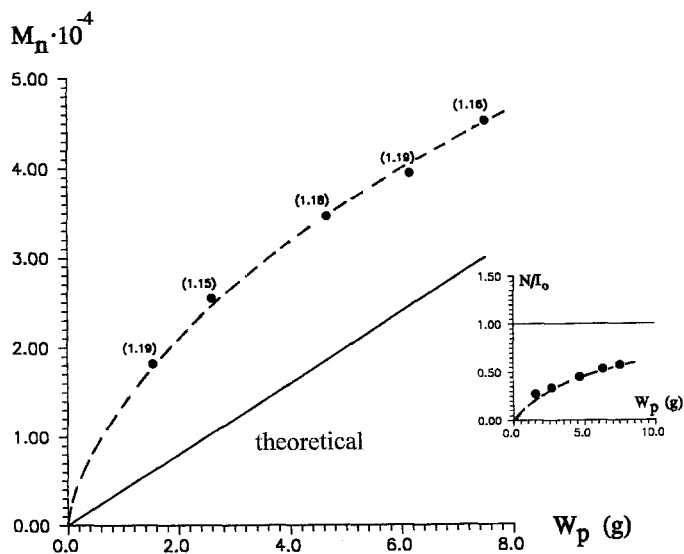


Figure 3. M_n and N/I_0 (inset) versus W_p plots obtained by the AMI technique for the 4-*tert*-butoxytoluene/ $TiCl_4$ /IB/*DtBP*/ CH_2Cl_2 :MeCHx 40/60 v/v/-78 °C polymerization system. $[I]_0 = 2.9$ mM, $[TiCl_4] = 45$ mM, $[DtBP] = 2.9$ mM; total volume = 99, 101, 103 and 105 ml corresponding to 4, 6, 8 and 10 ml IB added. Numbers in parentheses indicate M_w/M_n values.

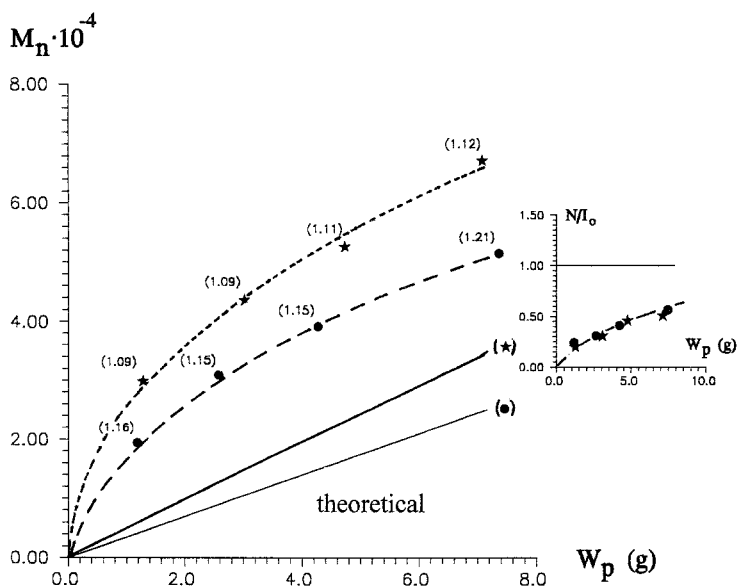


Figure 4. M_n and N/I_0 (inset) versus W_p plots obtained by the IMA technique for the 4-*tert*-butoxytoluene/ $TiCl_4$ /IB/*Di*BP/ CH_2Cl_2 :MeCHx 40/60 v/v/-78 °C polymerization system in the absence (x) of aging the initiating system ($[I_0] = 2.1$ mM, $[TiCl_4] = 48$ mM, $[DiBP] = 2.9$ mM) and with 30 mins aging (●) ($[I_0] = 2.8$ mM, $[TiCl_4] = 48$ mM, $[DiBP] = 3.1$ mM); total volume = 97 ml, $\Delta IB = 2$ ml, $\Delta t = 30$ min. Numbers in parentheses indicate M_w/M_n values.

The effect of solvent polarity on the initiating efficiency was investigated in a series of IMA experiments with 4-*tert*-butoxytoluene. As exhibited in Figure 5 increasing the CH_2Cl_2 /MeCHx ratio from 40:60 to 50:50, and to 60:40 v/v leads to increasing the initiating efficiency (I_{eff}) which reaches nearly 80% in the most polar solvent mixture. In these polymerizations PIBs with narrow MWDs ($M_w/M_n = 1.08 - 1.16$) were formed. Further increase of the CH_2Cl_2 content was also tested but in polymerization systems containing 67 and 75 v% CH_2Cl_2 precipitation of the polymer occurred, and PIBs with broad and bimodal MWDs were obtained. In these polymerization media I_{eff} increases to 85 % but control of MWD is not possible.

Analysis of the data obtained by the IMA experiments for the different initiators was carried out by the following equation derived for slow initiation in living carbocationic polymerization^(11,12,15):

$$j \frac{k_c}{k_p} \frac{[\Delta M]}{[I_0]} C_j = -\ln(1 - I_{eff}^j) - I_{eff}^j \quad (1)$$

where j is the number of monomer increments, k_c and k_p are the rate constants of cationation (initiation) and propagation, respectively, $[\Delta M]$ is the total amount of monomer added in an increment, $[I_0]$ is the initiator concentration, C_j is the apparent monomer conversion and I_{eff}^j is the initiator efficiency at j increments. In Figure 6, a

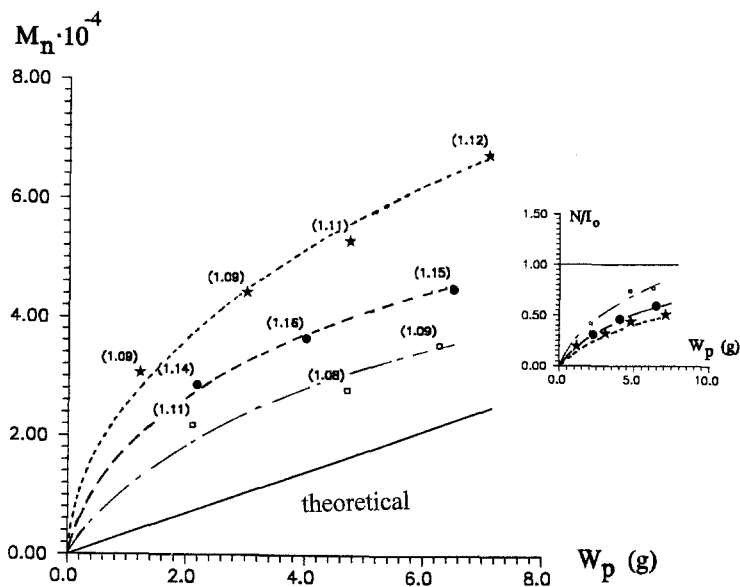


Figure 5. M_n and N/I_0 (inset) versus W_p plots obtained by the IMA technique for the 4-*tert*-butoxytoluene/ $TiCl_4$ /IB/*DtBP*/ CH_2Cl_2 :MeCH_x/-78 °C polymerization system with 40/60 (x), 50/50 (●) and 60/40 (□) v/v CH_2Cl_2 :MeCH_x ratios ($[I]_0 = 2.4$ mM, $[TiCl_4] = 47$ mM, $[DtBP] = 3.0$ mM); total volume = 96 ml, $\Delta IB = 3$ ml, $\Delta t = 30$ min. Numbers in parentheses indicate M_w/M_n values.

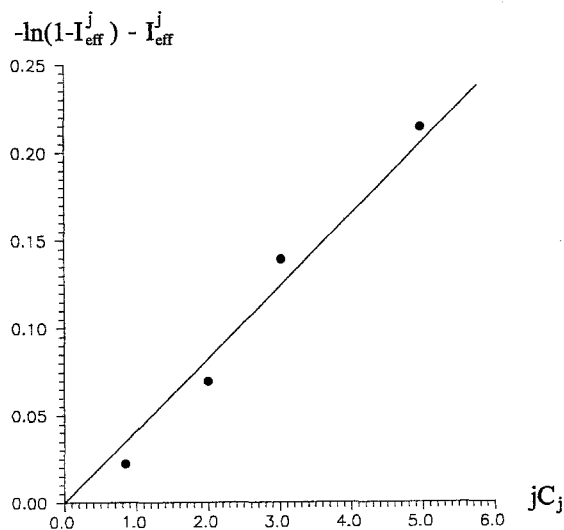


Figure 6. Plot of data obtained by IMA experiments with 4-*tert*-butoxytoluene according to equation 1 (see Figure 4 for experimental conditions without aging).

representative plot for 4-*tert*-butoxytoluene initiator is exhibited according to this equation. The straight line starting from the origin is in accordance with the kinetics of living polymerization with slow initiation. The ratio between the rate constants of initiation and propagation (k_c/k_p) can be determined from the slope of the straight line on the basis of eq. 1. With the exception of 4-*tert*-butoxyanisole similar straight lines were obtained by plotting the data according to equation 1 indicating living polymerization of IB with slow initiation by 4-*tert*-butoxybenzene and 4-*tert*-butoxytoluene in combination with TiCl_4 coinitiator. In the case of 4-*tert*-butoxyanisole an upward curvature was found in the slow initiation plot which might indicate that in addition to slow initiation chain transfer to the initiator also occurs as with dicumyl chloride in conjunction with BCl_3 coinitiator in CH_3Cl and CH_2Cl_2 solvents⁽¹⁴⁾.

Table 1. The k_c/k_p ratio for 4-*tert*-butoxybenzene and 4-*tert*-butoxytoluene initiators in polymerization of isobutylene (see Experimental and Figures for polymerization conditions).

Initiator	Solvent ratio $\text{CH}_2\text{Cl}_2/\text{MeCHx}$ (v/v)	$k_c/k_p \times 10^3$
4- <i>tert</i> -butoxybenzene	40/60	5.3
4- <i>tert</i> -butoxytoluene	40/60	3.5
	50/50	6.6
	60/40	7.8

Table 1 summarize the k_c/k_p values for 4-*tert*-butoxybenzene and 4-*tert*-butoxytoluene initiators under conditions used in this study. As data indicate in this Table, methyl substituent in the para position decreases the k_c/k_p ratio in the *tert*-butylphenoxy initiator. It is also clearly shown that polarity has a significant effect on the k_c/k_p values, i. e. increase of polarity increases the rate of initiation relative to that of propagation as it has been found with the 4-*tert*-butoxytoluene/ TiCl_4 initiating system. However, due to solubility problems of the resulting higher molecular weight polyisobutylene ($\sim 30,000$; see Figure 5) the volume fraction of the polar solvent (CH_2Cl_2) cannot be increased above 0.6 although according to the trend shown in Figure 5 and Table 1 further increase of polarity might lead to significantly higher (or near to theoretical) initiating efficiencies with the *tert*-butoxybenzene initiators.

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