Improvement in Alkoxide Anionic Initiation Technique by Using a Colorimetric Titration

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ABSTRACT: We developed a colorimetric method to follow and to control the complete transformation of an alcohol into an alkoxide. It was first tested on a small molecule and then extended to a macroinitiator. It allows us to obtain a final product without residual prepolymer and without side initiation due to an excess of carbanion. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1339–1343, 2005

Key words: anionic polymerization; colorimetry; initiatiors; living polymerization; titration

INTRODUCTION

Living anionic polymerization is a well-established method to control copolymer molecular weights and architectures, and to obtain low molecular weight distributions.[1] However, it needs very strict experimental conditions, especially a very high purity of the reagents and solvent.[2,3]

Even considering the precautions usually taken (experiments take place under inert atmosphere and reagents are carefully purified), the reaction medium is never 100% pure just before polymerization. This leads to the necessity of making a "zero point," which can be described as the neutralization of impurities of the reaction medium by an addition of a small amount of initiator.[4] The "zero point" is realized just before the addition of the necessary amount of initiator for the polymerization. The active form of the initiator is often colored; the difficulty lies in adding the initiator for the "zero point" until a very weak color is persistent. This visual estimation is very subjective, and often induces a slight excess of initiator. This excess is then cumulated with the necessary amount of initiator for the polymerization and inevitably leads to a difference between the expected and obtained molecular weight.

In the particular case where the polymerization is initiated from a prepolymer (for example, a hydroxy-terminated PEO), the "zero point" is not feasible. Indeed, the initiator transforms the prepolymer into an initiating species (for example, the transformation of alcohol into alkoxide) just after or at the same time as it purifies the reaction medium. Moreover, it is very difficult to visually appreciate this step, which can induce either a default of initiator, leading to unactivated prepolymer, or, an excess of initiator, leading to homopolymer formation. In both cases, a mixture of polymers is produced.

A colorimetric titration is a way to access directly to the equivalence, that is, the complete transformation of the alcohol into an alkoxide; in our particular case, *in situ* transformation of a hydroxy-initiator or -macroinitiator into an alkoxide for EO initiation. This way:

1. We get rid of the "zero point."
2. We avoid the problem of the imprecise concentrations of the various solutions (for example, due to a partial deactivation of the anions) .
3. It's not necessary to control the molecular weight of a commercial prepolymer before activation of the end groups.

Moreover, this titration was followed in real time, giving instantaneously the state of the system.

Taking advantage of the colors of the activating carbanions (respectively, deep green and red) and of their ability to transform a hydroxyl group into an alkoxide, we used naphthalene potassium (NaphtK) and diphenyl methyl potassium (DPMK), which are commonly used in anionic polymerization.

EXPERIMENTAL

Characterization

Size exclusion chromatography was carried out using a Waters 2690 liquid chromatograph equipped with three columns, Waters Styragel 5μm 10^4, 500, and 100

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TABLE I
Titration of 2 Phenylethanol (Experiments 1 and 2)

Characteristics	Experiment 1	Experiment 2
[Napht K] (mol/l)	0.547	
[DPMK] (mol/l)		0.652
Theoretical equivalence (ml)	0.43	0.36
Experimental equivalence (ml)	0.44	0.42

For all experiments: Volume of added Ph—CH$_2$—CH$_2$—OH: 1 ml. Concentration of the Ph—CH$_2$— CH$_2$—OH solution: 2.359 .10^{-1} mol/l.

Å (columns, injection, and refractometer temperature, 35°C; injection volume, 100 μL; solvent, THF 1 mL/min), and a refractive index detector (Waters 410). It was calibrated with PEO standards (194 to 124,700 g/mol).

UV–vis spectra of NaphtK and DPMK in THF were recorded on a Beckman DU 640 spectrophotometer.

The photometric titrations were carried out with a photometer 662, Metrohm, in a wavelength range from 400 to 700 nm.

Materials

Naphthalene (>99%, Aldrich, 91–20-3), diphenylmethane (99%, Aldrich, 101–81-5), potassium (≥98%, Riedel-de-Haën, 7440–03-7), and 2-phenylethanol (purum, Fluka, 6–12-8) were used as received. Ethylene oxide (>99.8%, Fluka, 75–21-8) was purified by cryodistillation. Tetrahydrofuran (>99%, Acros, 109–99-9) was distilled over CuCl$_2$ and sodium metal, degassed, and stirred over sodium metal in the presence of benzophenone until the violet color of the sodium benzophenone complex appeared.[5] THF was cryodistilled just before use.

Syntheses of the initiators

NaphtK and DPMK solutions were prepared according to the classical procedures.[6] Their concentrations, determined by acidic titration, were 0.547 and 0.652*M* (± 0.002*M*), respectively.

Titration of 2-phenylethanol

The reaction was carried out in a three-necked round bottom flask under dry nitrogen. One of the entrances was used to immerse the absorbance measuring probe (photometer 662) into the reaction medium.

50 mL of THF were first cryodistilled into the flask; the "zero point" was made visually. 1 mL of a solution, prepared with 0.28 mL of 2-phenylethanol in 9.72 mL of THF, were added into the flask under stirring. The initiator (NaphtK or DPMK) was progressively added via a microsyringe through a septum. The absorbance measure was conducted during the whole initiator addition.

Polymerization of ethylene oxide

Homopoly(ethylene oxide) or 2-phenylethanol was added to the cryodistilled THF. NaphtK or DPMK, respectively, was added to the solution while absorbance measures were recorded. As soon as the absorbance value was starting to increase significantly, the addition of initiator was stopped and the EO was poured dropwise into the solution. A detailed description of the EO polymerization procedure is given elsewhere.[7, 8]

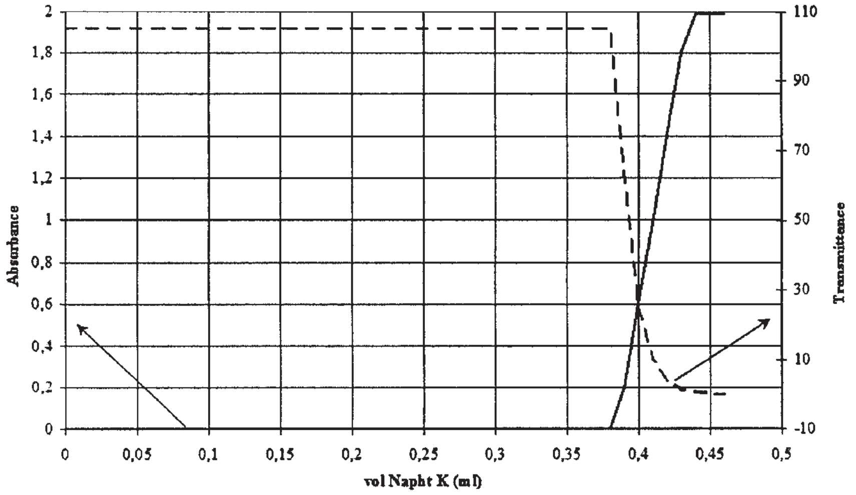

Figure 1 Absorbance and transmittance values at 700 nm during the titration of 2-phenylethanol with NaphtK (experiment 1).

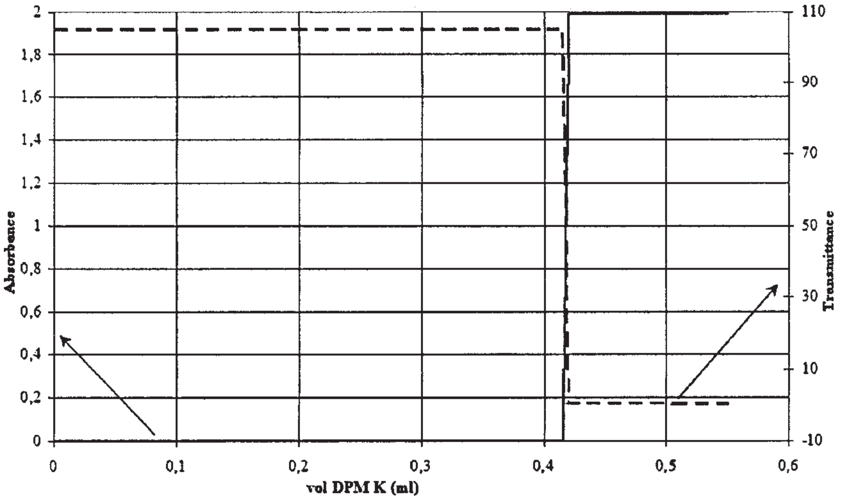

Figure 2 Absorbance and transmittance values at 420 nm during the titration of 2-phenylethanol with DPMK (experiment 2).

RESULTS AND DISCUSSION

Choice of wavelength for the measures

UV–vis spectra of the NaphtK and DPMK were recorded while adding increasing amounts of these initiators in THF.

Characteristic peaks of the NaphtK are located between 700 and 870 nm, and two peaks of lower intensity around 450 nm can also be pointed out. The characteristic peak of the DPMK is located between 405 and 475 nm. As the wavelength detection range of the used photometer was between 400 and 700 nm, we chose to follow the absorbance at 700 nm for the NaphtK and at 420 nm for the DPMK.

Titration of 2-phenylethanol

The first experiments were carried out intentionally making a visual "zero point" on the solvent, to point out the resulting error produced during the second step, that is, the titration. The "zero points" were carried out using 0.30 and 0.25 mL of NaphtK and DPMK solutions in experiments 1 and 2, respectively. The results obtained during the titration of the 2-phenylethanol are gathered in Table I and Figures 1 and 2. The absorbance variation appears clearly and spreads over a relatively short region. Assuming that the transformation of alcohol into alkoxide corresponds to the beginning of the variation of the solution absorbance, the equivalences of the titrations are reached for experimental volumes of 0.39 (NaphtK) and 0.42 mL (DPMK). The theoretical volumes necessary to titrate the alcohol after the "zero point" are 0.43 mL and 0.36 mL for the NaphtK and the DPMK, respectively. We noticed that the experimental volumes of the initiator solutions necessary to titrate the alcohol are relatively close to the theoretical values.

This error may be due to two phenomena:

1. A lack of precision in the concentrations of the solutions, since the solution of 2-phenylethanol was prepared in a cryodistilled volume of THF, in which the 2-phenylethanol was poured via a syringe. Then 1 mL of this solution was introduced into the reaction medium. The NaphtK and DPMK solutions were also prepared from cryodistilled THF. As a consequence, the concentrations of the various solutions (2-phenylethanol, NaphtK, and DPMK) are not precisely known.

TABLE II
Polymerization of EO (Experiments 3 and 4)

Characteristics		Experiment 3	Experiment 4
Alcohol to be activated		Ph—CH$_2$—CH$_2$—OH	PEO 6,000 g · mol^{-1} pdi = 1.09
Carbanion		DPMK	NaphtK
Mn PEO*	Expected	5,000 g.mol^{-1}	25,550 g.mol^{-1} (= 6,000 + 2 × 9,775)
	Experimental	4,800 g.mol^{-1}	24,100 g.mol^{-1}
Pdi*		1.09	1.15

*Determined by SEC in THF using a PEO calibration curve.

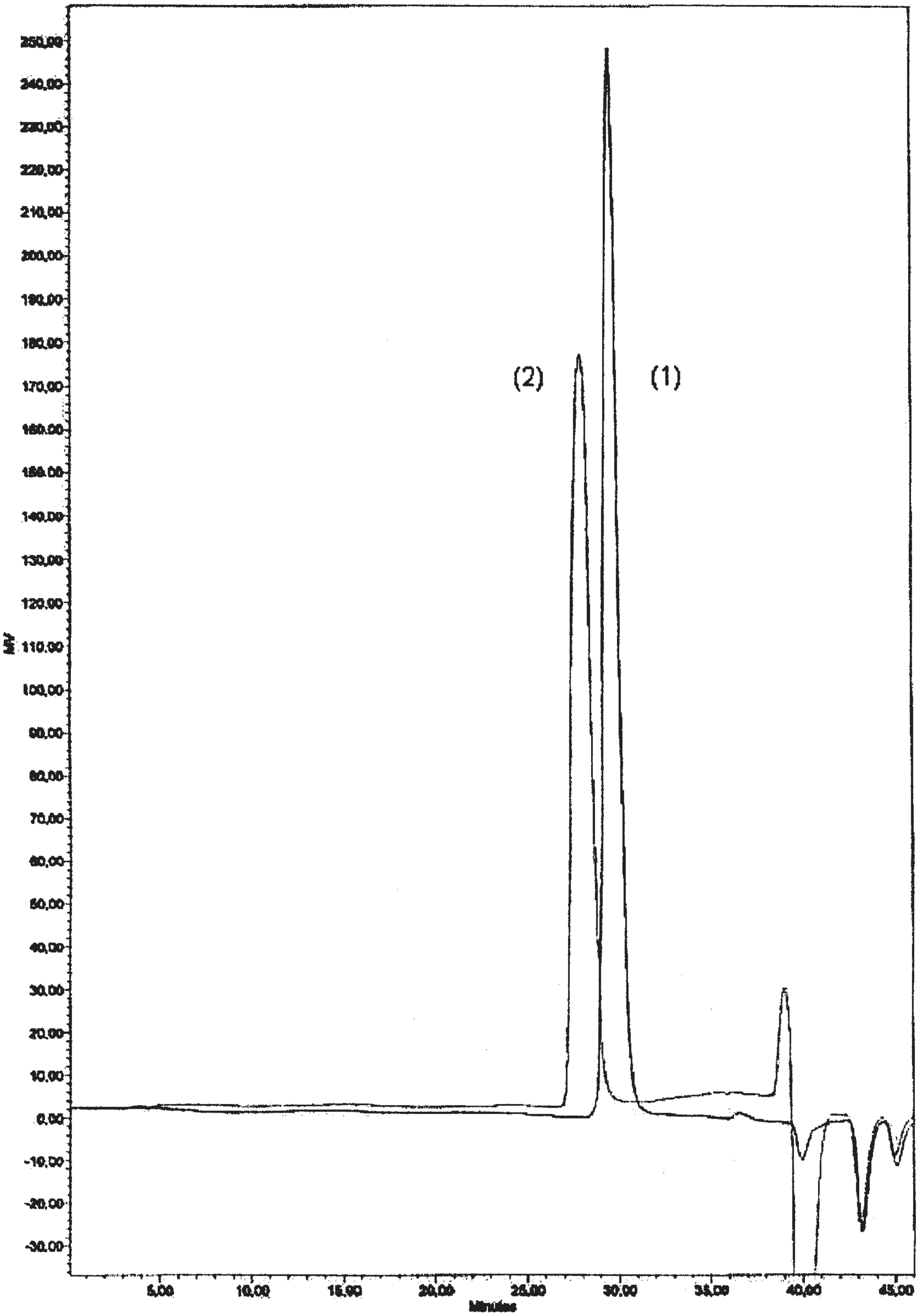

Figure 3 SEC chromatograms corresponding to experiment 4: (1) initial PEO; (2) final PEO.

2. The "zero point," carried out visually just before the titration, probably led to a slight excess of initiator.

By using an absorbance measurement, we avoid these two disadvantages and obtain a precise titration of the alcohol and we can assume that the experimental equivalence corresponds exactly to the titration of the alcohol in a pure medium.

As a consequence, it is neither necessary from now on to know the exact concentrations of the solutions, nor to carry out a visual "zero point" before the beginning of the experiment. The titration can be started from an impure medium.

Application to the synthesis of PEO from an alcohol and from a prepolymer

To validate the previous results, we applied the absorbance measurements to the activation of an alcohol followed by the polymerization of EO. No "zero point" was carried out previously.

Significant results are gathered in Table II and Figure 3:

Experiment 3 consists in the conversion of 2-phenylethanol into an alkoxide with DPMK to polymerize EO on this created active center.

What was applied to an alcohol in experiment 3 was then extended to a prepolymer in experiment 4, where the two terminal hydroxyl groups of a commercial PEO were activated with NaphtK. The generated alkoxides were used to polymerize EO and, as a consequence, the molecular weight of the PEO prepolymer increased.

The titration in experiment 3 was simply stopped when the absorbance and transmittance values at 420 nm started to vary. As expected, SEC of the product shows a very good agreement between experimental and expected molecular weight. Moreover, the polydispersity index of the final polymer is low.

The same conclusion applies to experiment 4. The polymerization was stopped after 24 h; the resulting weight yield reached 73%. SEC of the crude product shows an increase in molecular weight, a low polydispersity index, and no residual prepolymer, as well as no side homopolymer (Fig. 3). This means that all the alcohol groups have been quantitatively converted into alkoxides during the titration, and no excess of initiator was added. This colorimetric titration allows us to obtain a good polymerization control and the absence of homopolymer.

Application to the synthesis of the third arm of a star block copolymer

This synthesis is a very specific experiment that was carried out by some of the present authors.[9] The prepolymer used was a polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) (3000 PS and 3000 PEO g.mol^{-1}, pdi = 1.30) containing a hydroxyl group at the junction of the two blocks. It was activated with DPMK and followed by colorimetry. The alkoxide generated was used to polymerize *tert*-butylmethacrylate by reverse polymerization. The expected product is a triarm star block copolymer, PS-PEO-PtBuMA. A good initiation step was needed to obtain a pure triarm star block copolymer because no further purification of the triarm is possible. The final product has a real molecular weight of 48,000 g.mol^{-1}and a polydispersity index of 1.40.[9]

We can conclude that the macroinitiator was quantitatively activated and the initiation of tBuMA was complete. Neither homopoly(*tert*-butylmethacrylate) nor residual prepolymer can be detected. The polydispersity index given for the final product is rather low, compared to the initial copolymer polydispersity index and considering it is a complex-architectured copolymer. The final product is a well-defined high molecular weight triarm star block copolymer.

CONCLUSIONS

We have developed a technique that simplifies the anionic synthesis of a block copolymer and improves its reliability. We checked the efficiency of the technique on a small alcohol. The titration of an alcohol can be carried out from an impure medium, as the purification ("zero point") is done in the same step as the titration, and no good precision is needed in the concentrations of carbanion or alcohol solutions. Then we successfully applied this technique to the activation of prepolymers containing one or two blocks. The good quality of the following polymerizations allows us to conclude that the titration was carried out with a very good precision.

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