

A simplified procedure of anionic polymerization of styrene and dienes using 4,5-methylenephenanthrene as an indicator

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Summary

A titration method for quick and safe purification of solvents and monomers for anionic polymerization of styrene and dienes is presented. Protic impurities in the reaction-medium are removed by titration with butyllithium. The coloured carbanion of 4,5-methylenephenanthrene is used as an indicator to determine the end point of the titration. The titration is used in the synthesis of homopolymers and block copolymers of styrene and dienes with variable 1,2-polydiene content. Homopolymers and block copolymers in a large range of composition, molecular weight and with narrow molecular weight distribution were synthesized using the titration.

Introduction

One important prerequisite for living anionic polymerization is the complete absence of protic impurities and oxygen on a ppm scale. The common techniques for laboratory scale polymerization (breakseal, inert-gas) require much care in avoiding impurities. Pressure proof laboratory-reactor systems are often used, especially for diene polymerization, which allow a more simple and safer operation and polymerization on a larger scale. In most cases it is not possible to achieve a sufficient drying of the reaction-vessel by pre-heating. An additional drying step is required e. g. drying with metal-organic compounds. Cleaning of monomer, solvent and the reaction-vessel in separate steps is a time consuming step that often causes experimental errors. If all cleaning procedures can be carried out inside the reaction-vessel time is saved and more reproducible results should be obtained. We present a method to achieve the conditions for anionic polymerization by direct titration of the reaction-medium.

Experimental Part

Equipment

The polymerizations were carried out in a pressure proof reactor system with two separate reaction vessels. The temperature of the reaction vessels can be controlled from

- 80 °C to + 50 °C. The reactor system contains a tube with molecular sieve 4 Å which allows predrying of the butadiene and connections to vacuum and inert gas equipment.

A) Synthesis of polybutadienes with variable 1,2- content

The reaction vessel is predried by evacuation at 50 °C. 100 ml cyclohexane p. A. per 10 g butadiene, predried by storing some days over molecular sieve 4 Å, are added by a cannula. 10 mg (0.052 mmole) MPT per 100 ml solvent and the desired amount of dipiperidinoethane (DPE) are added. The solvent is degassed at 5 °C by evacuation up to the boiling point and ventilation with argon 3-5 times. The desired amount of 1,3-butadiene, predried over molecular sieve 4 Å, is dissolved in the solvent. The solution is titrated with *s*-BuLi until a yellow - orange colour appears and stays stable for at least 15 minutes. Depending on the content of DPE the colour fluctuates between a pale yellow (without DPE) and an intensive orange at high DPE contents. The calculated amount of *s*-BuLi for compensation of the MPT and initiation of the polymerization is added quickly. When the polymerization is completed it is terminated by adding methanol.

B) Synthesis of poly(styrene-block-butadiene)

The polybutadiene-block is polymerized as described in *A*). The styrene is destabilized by simple distillation and stored over molecular sieve 4 Å. The desired amount of styrene is added to cyclohexane p. A. containing 10 % absolute THF. The solution is degassed and titrated as described in *A*). When the intensive yellow-orange colour stays for at least 5 minutes, the MPT is compensated by adding exactly the calculated amount of *n*- or *s*-BuLi. The solution is pumped by a cannula to the living A-block under vigorous stirring under argon pressure. When the polymerization is completed it is terminated by adding methanol.

Titration of protic impurities in the presence of the monomers

In order to approach an efficient drying of monomer, solvent and reactor in one step it is recommended to carry out this procedure immediately before starting the polymerization. Consequently the reaction products have to remain in the polymerization solution and must not impair the polymerization. Therefore a sufficiently strong base is needed as a drying reagent whose conjugated acid does not terminate the polymerization reaction. A suitable base is *n*-butyl-lithium. Unfortunately when all protic impurities are removed it does initiate the anionic polymerization immediately. For an efficient control of the molecular weight the point where all protic impurities are removed has to be determined precisely. A promising approach is to use a compound that forms a coloured anion with butyl-lithium at the end point of the drying operation. For that purpose an indicator with the following properties is required:

1. clear and sufficiently quick colour change
2. no reaction with the monomer, no initiation of its polymerization
3. no influence on molecular weight, molecular weight distribution and microstructure
4. no reactions with the polymer, e. g. crosslinking
5. no colouring of the final polymer

Table 1 shows some compounds forming coloured anions with butyl-lithium:

Tab.1: investigated indicators

Indicator	Colour change	Reaction with monomers	additional problems
styrene	weak, too slow	yes	-
1,1-diphenylethylene	weak, too slow	dienes	-
triphenylmethane	only with polar solvents	no	-
benzophenone ¹	good	yes	side reactions during the polymerization reaction
fluorene	weak, too slow	no	-
2,3-benzofluorene	weak	no	side reactions with BuLi
4,5-methylene-phenanthrene	dependent on the solvent	no	-

¹ the titration was carried out with the red solution of BuLi/Benzophenone, the polymerization was started with s-BuLi

4,5-Methylenephenanthrene

With s-BuLi 4,5-methylenephenanthrene (MPT) forms a coloured carbanion:

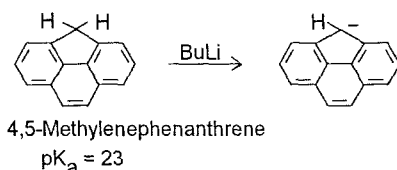


Figure 1 shows UV/VIS-absorption spectra of this anion, measured in different solvents:

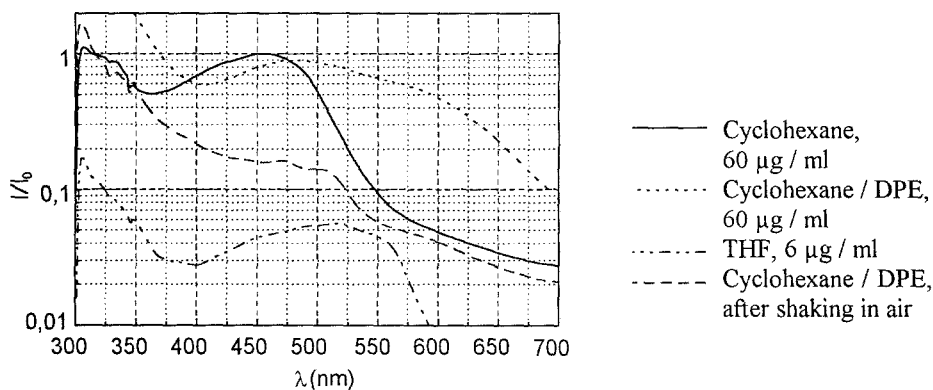


Fig. 1: UV/VIS-spectra of MPT⁻ in different solvents

An excess of s-BuLi was added to MPT. The spectra have been measured under argon. In cyclohexane a deep yellow-orange colour appears reaching its full intensity only after some minutes. By adding very small amounts of 1,2-dipiperidinoethane (DPE) the

adsorption is broadened towards the visible region. The colour appears much faster, facilitating the determination of the end point of the titration. In THF the solution immediately becomes deep red and the colour is stable over a long time below -20 °C, at room temperature it fades in a few minutes. By shaking the solution at the air the carbanion is oxidized to the likewise coloured ketone. Adding methanol to the living carbanion decolourizes the solution completely and reversibly.

Anionic polymerization in the presence of MPT

Because the anion of MPT (MPT⁻) remains in the reaction medium during polymerization, only monomers can be used which do not react with MPT⁻. Therefore methacrylates or more reactive monomers cannot be used. Suitable monomers are styrene and dienes like 1,3-butadiene and isoprene. In the following some examples are presented.

Polystyrene and Poly- α -methylstyrene

By the titration with MPT/BuLi polystyrenes and poly- α -methylstyrenes in a large range of molecular weights have been synthesized. In the polar solvent THF or in mixtures of cyclohexane and THF with a THF content of 50 % or higher the styrene monomer must be added when the titration is already completed. In these solvents the initiation of the styrene polymerization is so fast, that some styrene is initiated during the titration, which broadens the molecular weight distribution. Tab. 1 shows some polystyrenes and poly- α -methylstyrenes synthesized by this method. If apolar solvents like cyclohexane are used, the titration can be carried out in presence of the styrene monomer. There are no examples for the titration in presence of the styrene monomer in Tab. 2, but this method has been used extensively to purify solutions of styrene in cyclohexane/THF with 10 % THF for the preparation of AB- block copolymers. At this composition polymerization of styrene has never been observed during titration.

Tab. 2 Polystyrenes and poly- α -methylstyrenes

Polymer	Solvent	Mn (GPC)	U
PS 20	THF	20 000	0.06
PS 160	Cyclohexane/THF = 70/30	154 000	0.04
PS 240	Cyclohexane/THF = 70/30	230 000	0.04
PS 1.6 M	Cyclohexane/THF = 70/30	1 400 000	0.15
P- α -MS 44	THF	43 000	0.04
P- α -MS 60	THF	58 500	0.04
P- α -MS 100	THF	97 800	0.06

Cis 1,4-polyisoprene and polybutadiene with variable 1,2-content

1,3-butadiene can be polymerized to polybutadienes with variable 1,2-content up to 100% in presence of small amounts of DPE [1]. The 1,2-content is dependent on the molar ratio DPE/BuLi and the polymerization temperature.

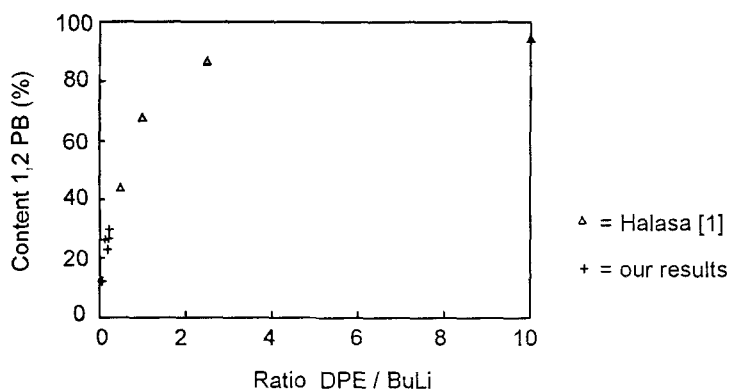


Fig. 2: 1,2-content of polybutadiene as a function of the ratio DPE/BuLi in cyclohexane at 50 °C

Table 3 shows the results of some polymerizations of 1,3-butadiene and isoprene in cyclohexane, carried out in presence of MPT. The solvent was cyclohexane p. a. which was degassed by evacuating several times at 0 °C. Butadiene (purity 99%) was predried over molecular sieve 4Å. Isoprene was degassed at -78 °C and destabilized by distillation.

Tab. 3 Synthetized polybutadienes and polyisoprenes

Polymer	Mn _{gpc}	U	DPE/BuLi	Temp. (°C)	1,2-content (%)
PB 110	110 400	0,06	1/13	50	12.3
PB 117	117 200	0.05	1/4.4	50	29.8
PB 76	76 100	0,05	1/7	20	68.0
PB 105	105 000	0.07	5/1	10	95.7
PI 3	172 600	0,08	-	20	5.0
PI 5	171 200	0,08	-	20	5.0

The lithium salts produced by the titration influence the polymerization rate. Furthermore the 1,2-content increases with increasing Li concentration [2]. Therefore an uncertainty in prediction of the 1,2-content of more than 10 % results, if very high amounts of water are removed by the titration. This can be avoided by keeping the cyclohexane over molecular sieve 4Å for some days and predrying the butadiene with molecular sieve. No additional purification steps have been used. High molar masses could be realised with very small polydispersities. In the case of the polymerization of butadiene the 1,2-content could be varied in a large range.

The polymerization of the polyisoprenes was carried out without DPE in order to achieve a high cis 1,4-content.

The titration with MPT/BuLi is not sufficient for anionic polymerization in THF. THF has to be purified by distillation over sodium/benzophenone, otherwise it is not possible to get a stable colour with MPT/BuLi, even at low temperatures. For the polymerization of 1,3-butadiene in THF it was further necessary to dry the butadiene monomer over pure n-BuLi (without solvent) due to an impurity with very low acidity. This impurity does not influence the polymerization of butadiene in cyclohexane, presumably due to a shift of

the scale of acidity in this solvent, but in THF it terminates the polymerization. The impurity cannot be removed by titration with MPT/DPE. Also the conventional procedure of distilling the butadiene from dibutylmagnesium was not successful. The polymerization of butadiene was only possible with butadiene dried over pure n-BuLi and use of predestilled THF. If the polymerization of butadiene is carried out in presence of MPT, the polymerization rate is strongly reduced (ca. 100 times). The effect is very similar to the effect that occurs when the polymerization is carried out in presence of lithium-alkoxides [3]. The molecular weight distribution for the polymerization of butadiene in THF is not affected by the presence of MPT.

AB- Block copolymers with variable 1,2-content

The common way to obtain polystyrene/polybutadiene AB- block copolymers with high 1,2-content is anionic polymerization in THF at -78°C . The disadvantages of this method are the necessity of extensive purification procedures and the limitation to a maximum 1,2-content of ca. 94 %. In contrast the use of apolar solvents like cyclohexane and DPE as modifier offers access to a wide range of 1,2-content up to 100 %. In this system the purification by MPT/BuLi can be applied, without any further preparations.

Using this method the polymerization must be started with the polybutadiene block. When styrene is polymerized in presence of DPE side reactions occur, which heavily broaden the molecular weight distribution. In the presence of DPE it is also not possible to reach a satisfactory transfer step from the growing polystyrene anion to the butadiene monomer. Only between 5 and 15 % of the butadiene monomer are consumed. A bimodal molecular weight distribution is obtained with a main peak at the molecular weight of the A-block and a very broad second peak of higher molecular weight, containing some butadiene. This behaviour is independent of the presence of the anion of MPT. The problem can be circumvented by starting the polymerization with butadiene and adding 10% THF to the solution of the styrene monomer. Furthermore this sequence is necessary to avoid solubility problems which occur in cyclohexane with polystyrene of high molecular weight. Tab. 4 shows some polymers prepared by this method.

Tab. 4 Poly(styrene-block-1,2-butadiene) (SB) and Poly(styrene-block-isoprene) (SI) block copolymers. All SB polymers have a 1,2-content of 100%.

Polymer	Solvent	M_n (GPC)	U	Weight% Polydiene (NMR)
SB 55	Cyclohexane	55 300	0.03	16.3
SB 77	Cyclohexane	77 100	0.03	10.1
SB 115	Cyclohexane	115 900	0.03	15.1
SB 170	Cyclohexane	170 000	0.05	55.0
SB 80	THF	80 000	0.03	73.7
SI 33	Cyclohexane	33 000	0.04	87.5
SI 60	Cyclohexane	60 000	0.05	87.0

The GPC-measurements have been made using a polystyrene-standard. For the PB-block M_n (GPC) was corrected by a relationship which was obtained from osmometry [4].

Fig. 3 shows GPC-curves of some synthesized polymers.

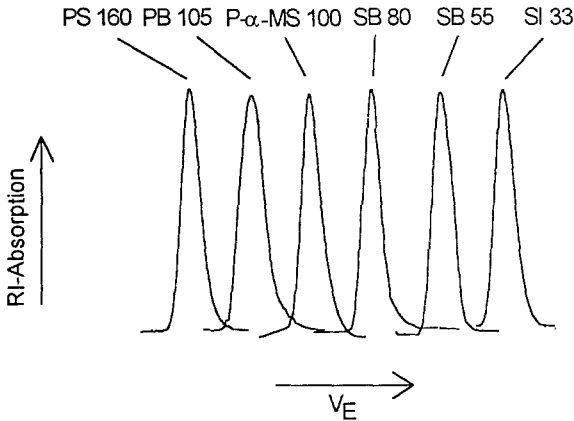


Fig. 3 GPC -curves of some synthesized polymers

Triblock copolymers poly(styrene-block-1,2-butadiene-block-styrene)

In cyclohexane/DPE the transfer step from the polystyryl anion to the butadiene monomer does not work satisfactorily. This problem occurs for sequential polymerization and probably also for difunctional initiators which are commonly derived from styrene [5,6]. That this behaviour is caused by the modifier DPE and not by the titration indicator MPT is demonstrated by the following experiment.

An average number of two units butadiene per chain was polymerized on the living A-block (polystyrene) in absence of DPE. After a reaction time of 2 h the main quantity of butadiene was added together with DPE. When the polymerization of butadiene was completed, a sample of the AB- blockcopolymer was taken and terminated. A third block (polystyrene) was polymerized on the living AB- blockcopolymer. Apart of the main peak with the calculated molecular weight for the triblock copolymer the molecular weight distribution of this polymer shows two further peaks, a bigger one with the calculated molecular weight for the A-Block and a smaller one with higher molecular weight.

The main peak proves the effect of the "capping" of the polystyrene A-block with butadiene in absence of DPE. The capped chains grow with a narrow molecular weight distribution. The two other peaks are caused by chains, which not have been capped by statistical reasons. The resulting molecular weight distribution of these chains is similar to that obtained by polymerizing an AB- diblock copolymer poly-(styrene-b-butadiene) with DPE, beginning with the styrene monomer. The bigger peak with a molecular weight as calculated for the A-block consists of pure polystyrene, which could be proved by extraction with acetone. Acetone extracts selectively polystyrene, it does not dissolve SB-block copolymers. The other peak contains some additional butadiene. Fig. 4 shows the GPC-curves discussed above.

The GPC-curves for the triblockcopolymer and for the sample, which was taken, when the polymerization of the two first blocks is completed, show no difference in shape (the GPC-curve of the AB- block-sample is not shown in Fig. 4). The main peak of the triblockcopolymer is shifted to the calculated molecular weight of the third block. The two other peaks are not shifted. Therefore the process which hinders the transfer step from styrene to butadiene is a kind of termination.

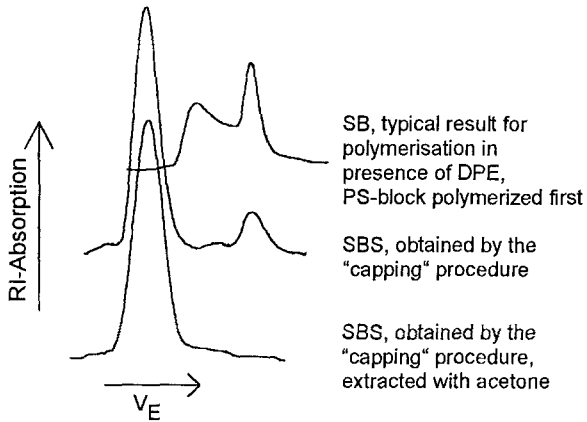


Fig. 4. GPC curves showing the "capping"-procedure.

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