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INFLUENCE OF UV LIGHT WAVELENGTH ON GRAFTING OF PVC

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Key Words: Living radical polymerization; Grafting; UV absorption

ABSTRACT

PVC-(*n*-propyl xanthate) macroinitiators (PVC-*n*PX) with different fractions of xanthate groups were synthesized in THF/acetone solutions from PVC and potassium *n*-propyl xanthate (*n*PX). Methyl methacrylate (MMA) was grafted onto PVC-*n*PX macroinitiators using UV light of 254, 302, and 366 nm at 20 and 40°C. Reaction time was 1, 3, or 5 hours. Graft copolymerization and UV homopolymerization took place at the same time. Grafting was the most effective at a wavelength of 302 nm with a weight gain of copolymerization of up to 45%. The grafted copolymers were separated from the mixture by selective precipitation of THF solutions with hot ethanol and extraction with hot ethanol. The mechanism of grafting is discussed on the basis of the molecular weight of copolymers, on the quantity of homopolymers, on the structure of copolymers, and on the UV absorption of end groups.

INTRODUCTION

In previous work [1, 2] we reported that living graft polymerization is applicable to a large number of chloropolymers. Due to its satisfactory solubility in organic solvents suitable for grafting, the most convenient chloropolymer is PVC. Grafting is a two-step procedure. In the first step the chlorine atoms of PVC react with water-soluble thio compounds such as potassium xanthate, potassium diethyldithiocarbamate, and potassium mercaptobenzthiazole to form macroinitiators with active thio functionality on the chain [3, 4]. In the second step, UV light decomposes the macroinitiators into macroradicals and primary thio radicals which can further react with various monomers to form graft copolymers or homopolymers. The aim of this work is to determine the influence of UV wavelength on the yield of graft polymerization and on the molecular weight of copolymers.

EXPERIMENTAL

Materials

PVC was a product of Wacker C65V (K value 65, $M_n = 65,000$ g/mol), and methyl methacrylate (MMA) was a product of Rohm and Hass. Potassium *n*-propyl xanthate was prepared from *n*-propanol, CS_2 , and KOH in ethanol/water solution at 20°C. All chemicals and solvents used in this work were purified and dried before use.

Synthesis of Macroinitiators

The PVC-(*n*-propyl xanthate) macroinitiators (PVC-*n*PX) with various amounts of xanthate groups were synthesized from PVC and potassium *n*-propyl xanthate. PVC (80 g) was dissolved in 450 g of THF. Potassium *n*-propyl xanthate (*n*PX) was dissolved in a 250-g mixture of acetone and THF (1:1). Solutions with different portions of PVC and *n*PX were mixed and thermostated at 40°C for a given reaction time. Macroinitiators were precipitated in distilled water, dried, and purified three times by reprecipitation from THF into water. The degree of substitution of chlorine atoms of PVC by xanthate groups was determined using a Varian DMS 80 UV-VIS spectrophotometer in the 200 to 400 nm range. Macroinitiators and copolymers were dissolved in THF at a concentration of 0.5 mg/g. Homopolymers were dissolved in a concentration of 1.25 mg/g. For quantitative determination of the grafted xanthate groups, the absorption of *s*-methyl-*o*-ethyl xanthate ($\lambda = 278$ nm, $\epsilon = 11,300$ L·mol⁻¹·cm⁻¹) was used.

Grafting of Macroinitiators with MMA

Three different macroinitiators with 0.54, 0.86, and 1.30 mol% of bonded xanthate groups were used for grafting. The macroinitiators were dissolved in THF and mixed in a quartz reaction vessel with MMA at a weight ratio of 1:5. The solutions were stirred magnetically under nitrogen at constant temperatures of 20 and 40°C. The solutions were irradiated from the top of the reaction vessel at 4 cm distance from the solution with a UV lamp at 254, 302, and 366 nm. The graft

polymerizations were run for 1, 3, or 5 hours. After the reaction was finished, the polymerization product was precipitated in methanol and dried. The weight gain of polymerization (homo and grafted copolymer) was calculated from the weight increase. The PMMA homopolymers were separated from the mixture by selective precipitation of the grafted PVC from hot THF solution with hot ethanol and subsequent Soxhlet extraction with hot ethanol for 48 hours. The gain of copolymerization (grafted copolymer) was calculated from the weight differences before and after extraction. For determination of structure, number, and length of grafted chains, ^1H - and ^{13}C -NMR spectroscopy were used. The molecular weights were measured by GPC on PL-gel mixed columns using THF as the solvent. To remove crosslinking products before measurement, the samples were filtered through $0.2\ \mu\text{m}$ Teflon filters.

RESULTS AND DISCUSSION

Synthesis of Macroinitiators

In the first step of the reaction, the nucleophilic substitution of PVC chlorine with potassium xanthate takes place mostly on the meso position of the PVC chain by a stereospecific $\text{S}_{\text{N}}2$ mechanism [5-8]. Besides substitution, decomposition of xanthate and crosslinking of the formed macroradicals are possible. The degree of substitution was followed by UV and ^1H -NMR measurements. The UV absorption of PVC-*n*PX increases with increasing reaction time and with a higher number of bonded xanthate groups. Two maxima can be seen in the spectra (Fig. 1): The signals at 280 and 336 nm of the xanthate group belong to the corresponding groups of crosslinking side reactions. Crosslinking increases with an increasing degree of

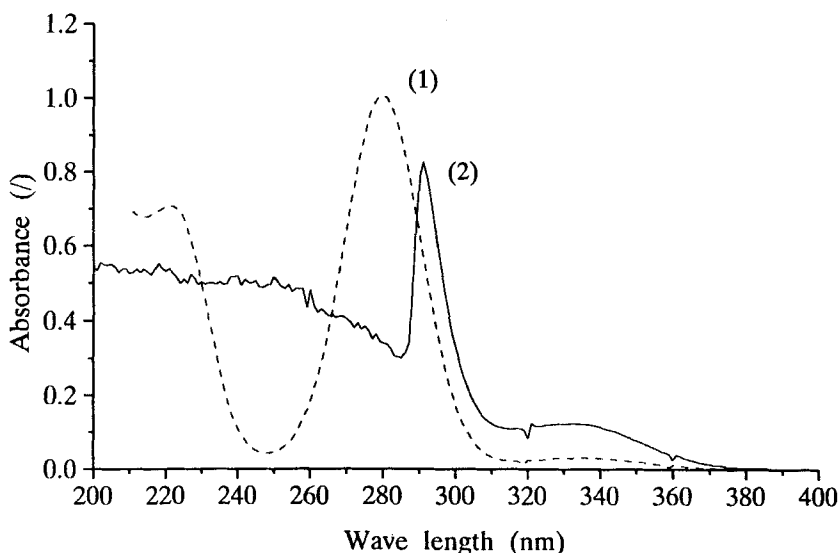
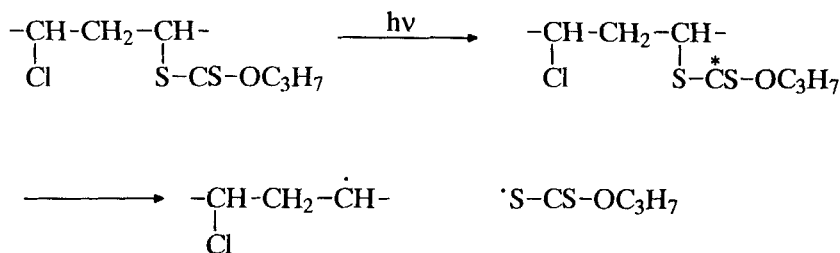


FIG. 1. UV spectra of PVC-*n*PX with 0.54 mol% of *n*PX in THF (1) and in THF/MMA solution (2).



SCHEME 1.

substitution of the xanthate groups. The crosslinked products were separated from the macroinitiators before the use of macroinitiators.

Grafting of Macroinitiators with MMA

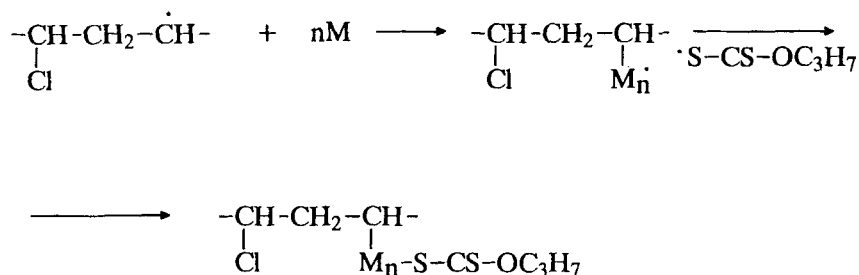
The irradiation of the macroinitiator with UV light, which is absorbed in the *n*PX groups, leads to excitation and further decomposition of *n*PX groups. The mechanism is the same as the decomposition of molecules containing the C=O bond and is known as the Norrish II mechanism [9]. The most efficient wavelength for decomposition can be determined by measuring the UV spectra in the polymerization media (monomer, solvent). The reactions proceed at the highest rate at the peak absorption wavelength [10] (Scheme 1).

The macroradicals formed at decomposition can react with monomer by two different mechanisms.

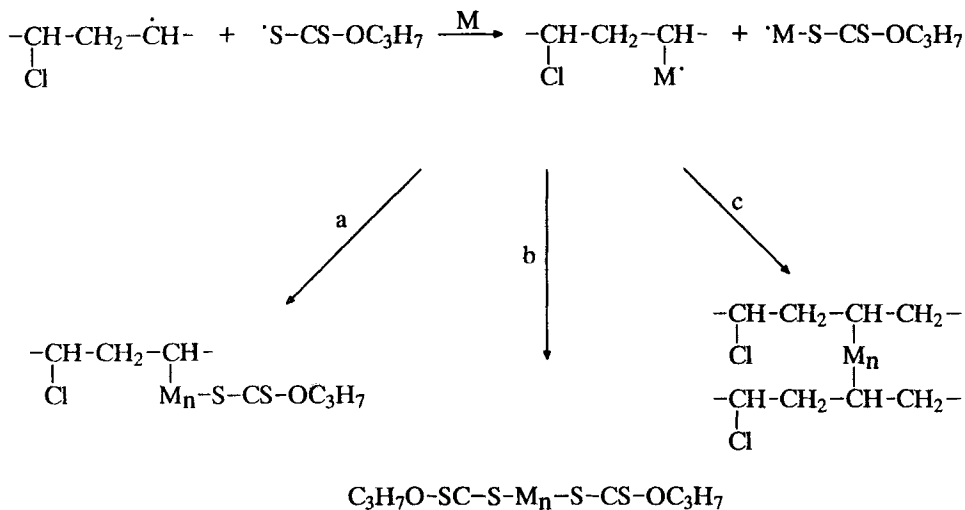
In the first mechanism the macroradical reacts with the monomer until termination with the primary radical stops the propagation. The copolymer has a xanthate end group and is therefore capable of further copolymerization (Scheme 2).

In the second mechanism the xanthyl radicals react with monomers to form homo macroradical. Therefore, two different macroradicals are formed, i.e., a grafted and a homo macroradical. By combination termination of those two macroradicals or a primary radical, three different types of macromolecules can be obtained (Scheme 3).

At the termination of the grafted macroradical and of the homo macroradical by a xanthyl radical, chains with xanthate end groups are formed. The copolymers



SCHEME 2.



SCHEME 3.

are similar to those obtained by a pseudo-living mechanism [11] and are therefore capable of further copolymerization. At the termination of two homo macroradicals, a homopolymer having two xanthate groups at the chain ends is obtained, and it is capable of further homopolymerization. At the termination of two grafted macroradicals a crosslinked copolymer is obtained. PVC, which lost the active xanthyl radical, is capable of initiating the homopolymer or terminating the macroradicals.

UV radiation of the monomers also enables other reactions like photo homopolymerization to take place. The photo-initiated homo macroradical can be terminated with a grafted macroradical or other homo macroradical.

The rate of grafting depends on the number of bonded xanthate groups, on the UV wavelength, and on the reaction temperature. The results are given in Tables 1 and 2.

The copolymerization weight gain is proportional to the rate of grafting. At a lower number of bonded xanthate groups, the copolymerization weight gain increases intensively with the reaction time, while with a higher number of bonded xanthate groups the increase becomes slower. The macroinitiator with a higher number of xanthate groups is partly crosslinked. Due to the steric hinderance, the crosslinking prevents the grafting of individual reactive positions. It was also found that impurities formed by the decomposition of potassium xanthate during the synthesis of macroinitiator decrease the rate and weight gain of copolymerization. Due to branching and partial crosslinking of the macroinitiators with a higher number of xanthate groups, the solutions were highly viscous. Therefore, purification was less efficient and copolymerization weight gain was lower.

Determination of End Groups by UV Measurements

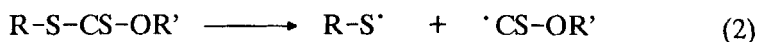
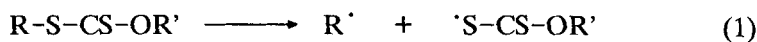
Besides ^1H and ^{13}C NMR, UV measurements were used for determination of the xanthate end groups. There are two possible mechanisms of decomposition of PVC-*n*PX macroinitiator:

TABLE I. Dependence of the Weight Gain of Polymerization and Copolymerization of PVC-*n*PX and MMA on Wavelength, on Reaction Time, and on the Quantity of Xanthate Group. $T = 40^{\circ}\text{C}$

	Reaction time, hours	$\lambda = 254 \text{ nm}$			$\lambda = 302 \text{ nm}$			$\lambda = 366 \text{ nm}$		
		Weight gain, %	Gain in copolymerization %	Gain in copolymerization, %	Weight gain, %	Gain in copolymerization, %	Gain in copolymerization, %	Weight gain, %	Gain in copolymerization, %	Gain in copolymerization, %
PVC-0.54X	1	14.1	/	/	16.8	/	/	15.6	/	/
	3	42.0	13.4	37.4	65.8	37.4	55.0	26.7	26.7	26.7
	5	65.5	18.8	51.7	99.4	51.7	96.5	41.9	41.9	41.9
PVC-0.86X	1	15.4	/	/	33.7	/	23.6	/	/	/
	3	47.7	13.6	43.3	87.0	43.3	63.3	31.6	31.6	31.6
	5	65.9	16.8	65.1	126.4	65.1	101.5	47.2	47.2	47.2
PVC-1.3X	1	20.2	/	/	26.6	/	22.8	/	/	/
	3	55.4	15.6	38.6	76.8	38.6	62.3	26.8	26.8	26.8
	5	83.0	28.7	58.7	115.4	58.7	107.3	54.6	54.6	54.6

TABLE 2. Dependence of the Weight Gain of Polymerization and Copolymerization of PVC-*n*PX and MMA on Wavelength, on Reaction Time, and on the Quantity of Xanthate Group. *T* = 20°C

	Reaction time, hours	$\lambda = 245 \text{ nm}$		$\lambda = 302 \text{ nm}$		$\lambda = 366 \text{ nm}$	
		Weight gain, %	Gain in copolymerization, %	Weight gain, %	Gain in copolymerization, %	Weight gain, %	Gain in copolymerization, %
PVC-0.54X	1	2.9	/	10.8	/	7.6	/
	3	13.7	/	37.1	17.5	27.6	11.5
	5	28.4	7.4	63.8	29.5	48.4	22.1
PVC-0.86X	1	7.6	/	17.0	/	12.0	/
	3	13.5	3.5	45.9	24.2	35.8	17.0
	5	37.1	10.0	70.4	35.8	55.7	27.5
PVC-1.3X	1	9.9	/	18.5	/	14.7	/
	3	17.0	/	40.9	20.4	38.6	18.7
	5	34.4	7.0	61.3	29.1	57.0	25.4



The measured NMR and UV spectra of end groups of grafted copolymers are similar to the spectra of the macroinitiator. Therefore, we conclude that the decomposition of xanthate groups takes place according to Mechanism (1). The total number of xanthate units did not change during grafting. We can see this from UV absorption of the individual products of polymerizations. Their absorption decreases linearly with an increasing share of MMA segments in homo and copolymer, and it is proportional to the content of xanthate groups (Fig. 2, Line 1). The line is calibrated from the absorption of PVC-*n*PX using the samples with different contents of xanthate groups and PMMA prepared by ionic polymerization which has no xanthate groups. After separation of the products of polymerization as homopolymer and grafted copolymer, both compounds still show UV absorption. The absorption of copolymer is lower than it should be according to the content of monomer units of the side chains between xanthate groups and PVC backbone (Lines 2a and 2b). Some of the primary radicals reacted with monomers to form homopolymers with xanthate groups according to Scheme 3 and some of the side chains were terminated with other nonliving radicals which did not absorb the UV light.

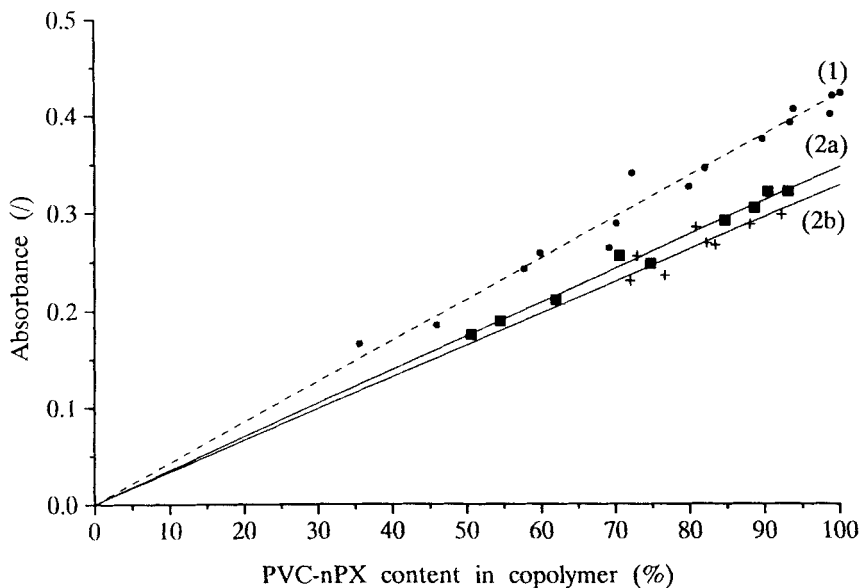


FIG. 2. Dependence of UV absorbance on the macroinitiator content. Products of polymerization (1). Copolymers synthesized at 366 nm (2a) and at 302 or 254 nm (2b).

Influence of the Wavelength on Grafting

The copolymerization weight gain depends mostly on the wavelength of UV light. The copolymerization weight gain increases with increasing grafting time, number of xanthate groups, and temperature (Tables 1 and 2). At 302 and 366 nm the copolymerization weight gain is up to 50%, while at 254 nm it is only up to 25%. In all cases other than grafting, PMMA homopolymers are formed.

Since the rate of the photochemical reaction depends on the intensity of the absorbed light and on the excitation of the macroinitiator reactive groups, the highest efficiency of graft copolymerization appearing at 302 nm can be explained on the basis of the UV absorption spectra of macroinitiators and MMA measured in THF solution (Fig. 1). The xanthate group absorbs between 248 and 310 nm. The absorption is stronger at 302 than at 254 nm, and therefore the rate of graft copolymerization is more efficient at a higher wavelength. By comparing the copolymerization weight gain at 254 nm with that at 366 nm, we can see that at 254 nm the copolymerization is less efficient although the absorbance of macroinitiator is stronger. The solution of a mixture of macroinitiator and MMA absorbs between 200 and 380 nm. The xanthate groups in this solution absorb between 284 and 310 nm, with the maximum at 291 nm. MMA has a strong continuous absorption from 200 to 300 nm. A part of the UV light is absorbed by MMA and can initiate homopolymerization. Therefore, polymerization using 254, 302, and 366 nm wavelengths cannot only be a consequence of excitation of the xanthate group. The energies of those values are strong enough (254 nm = 471 kJ/mol, 366 nm = 327 kJ/mol) to break a weak C–S bond (280 kJ/mol), produce radicals, and start graft copolymerization. At the 366 nm wavelength, the energy of excitation is close to the energy for breaking the C–S bond, absorption of MMA is minimal, and almost all the light is used to break the C–S bond. Therefore, the grafting proceeds more efficiently than with stronger 254 nm light.

Molecular Weight of Grafted Copolymers

The molecular weights for homo- and copolymers were determined. Besides homo- and copolymerization, crosslinking also took place. The copolymers consisted of soluble low branched chains and of insoluble crosslinked products. To separate the insoluble microgel, all samples were filtered through a 0.2- μ m Teflon filter. The molecular weights of the copolymers increase linearly with increasing reaction time and conversion (Table 3). Due to the living character of the growing macroradical, the molecular weights are, on average, largest at the highest rate of copolymerization and at the highest conversion.

The molecular weight, the rate of graft copolymerization, and the weight gain of grafting have maximal values at 302 nm, which was the most appropriate wavelength for the grafting of PVC. The molecular weights of homopolymers also increase with the reaction time and are lower than those of copolymers.

Second Step of Polymerization

Otsu et al. [11, 12] predicted a pseudoliving character of polymerization by thio and xanthate initiators. An important criterion for pseudoliving polymerization is the ability of the isolated graft copolymer from the first step of polymerization to

TABLE 3. Comparison of the Molecular Weight and Average Number of Segments of Side Chains of Copolymer after the First and the Second Steps of Grafting

After first step of grafting			After second step of grafting		
M_n , g/mol	Average length of side chains	M_w/M_n	M_n , g/mol	Average length of side chains	M_w/M_n
84,170	40	2.431	96,150	65	2.676
73,550	18	2.515	93,900	60	2.462
80,870	33	2.601	99,540	72	2.724
89,800	52	2.775	100,360	74	2.706
82,160	36	2.357	88,780	49	2.583
74,610	20	2.622	86,920	46	2.643

be used as a macroinitiator for the second step of graft copolymerization in which longer side chains are formed. Xanthate groups on the side chains can be split into grafted macroradicals and xanthyl radicals. To confirm the grafting, some of the purified grafted copolymers were used as macroinitiators in a second polymerization step using a similar procedure for grafting as in the first step. The molecular weights of all copolymers increased after the second polymerization step. Number, length, and molecular weight of the grafted chains were calculated from the ratio of MMA and xanthate groups in $^1\text{H-NMR}$ spectra and from UV and GPC measurements. The average number of grafted chains used for grafted macroinitiator was 4.8 chains per macromolecule. After the second step of grafting the number of grafted chains was the same but the length of the side chains had increased. The average lengths of grafted MMA monomers were between 18 and 52 monomer units before the second step. After the second step of grafting the side chains had increased up to 74 monomer units. The increase of side chains is shown in Table 3.

CONCLUSION

The xanthate group is an efficient UV initiator for pseudoliving radical graft copolymerization. The reaction is fastest at a wavelength of 302 nm with a gain of copolymerization up to 45%. The lower grafting at 254 nm can be explained by photo homopolymerization of the monomer. On the basis of the measured UV spectra of the mixture of macroinitiator, solvent, and monomer, the most efficient wavelength for grafting can be predicted.

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