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Analysis of poly(chlorophenyl methacrylates) by ultraviolet spectroscopy

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Summary

A number of copolymers of methyl methacrylate and chlorophenyl methacrylates of different structure was prepared and analyzed by ultraviolet spectroscopy. It was found that the copolymer composition can be determined using a calibration curve based on mixtures of the appropriate homopolymers. The U.V. spectroscopical results are in good agreement with the chlorine analysis.

INTRODUCTION

Halophenyl methacrylate polymers and copolymers possess a high radiation sensitivity and can be used as resist materials in E-beam lithography /1/. The investigation of their electron beam sensitivity revealed a crosslinking mechanism via chlorine elimination. The competing decomposition reactions are influenced by the number and position of the chlorine substituent /2/. Therefore reliable information on the fine structure of these products is of key importance.

There are a number of methods for analysis of copolymers, including infrared spectroscopy, NMR, elemental analysis and U.V. spectroscopy. However, examples of bias in copolymer analysis have been reported /3,4/ and the suitability of a particular method has to be proven for each single case.

EXPERIMENTAL

The polymers were prepared according to the following general procedure:

The methacrylate monomers were synthesized by reaction of methacryloyl chloride and the corresponding chlorophenol. The polymers were prepared by dibenzoyl peroxide initiated radical polymerization of the monomers in benzene at 80 °C

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*To whom offprint requests should be sent for about 20 hours. The polymers were isolated by pouring the reaction solution into methanol and purified by reprecipitation.

The composition of the monomer mixtures is summarized in Table 1.

The ultraviolet spectra were recorded on a Carl Zeiss Jena UV/VIS spectrometer M40 using THF as the solvent. The number average molar masses were determined in DMF using a membrane osmometer KNAUER.

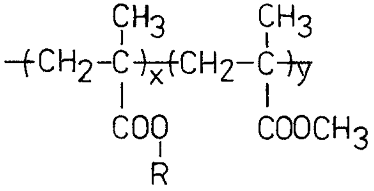
Table 1: Summary of the Polymerization Experiments

Sample	ClPh-MA	Comonomer Amount ClPh-MA mmole(mole%)	Comonomer Amount MMA mmole(mole%)	$\overline{M_n} \times 10^5$
1	2-ClPh-MA	150 (100)	---	1,24
2	2-ClPh-MA	100 (50)	100 (50)	2,12
3	2-ClPh-MA	100 (50)	100 (50)	1,25
4	3-ClPh-MA	50 (100)	---	1,51
5	3-ClPh-MA	80 (50)	80 (50)	1,29
6	3-ClPh-MA	30 (41)	43 (59)	0,93
7	4-ClPh-MA	460 (100)	---	3,35
8	4-ClPh-MA	50 (50)	50 (50)	2,90
9	4-ClPh-MA	130 (25)	380 (75)	2,23
10	2,4-ClPh-MA	45 (100)	---	1,37
11	2,4-ClPh-MA	50 (50)	50 (50)	0,90
12	2,4-ClPh-MA	55 (28)	145 (72)	1,68
13	2,4-ClPh-MA	35 (18)	165 (82)	1,68
14	2,4,6-ClPh-MA	30 (100)	---	-

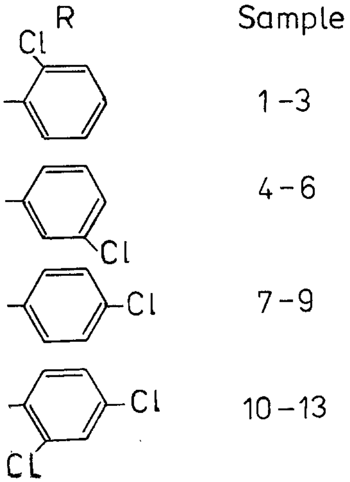
ClPh-MA = Chlorophenyl methacrylate

RESULTS AND DISCUSSION

In order to investigate a wide variety of polymers chlorophenyl methacrylates of different chemical structure were copolymerized with methyl methacrylate in various ratios.



$$-\!\!\left(CH_2-\underset{\underset{\underset{R}{|}}{COO}}{\overset{CH_3}{C}}\right)_{\!x}\!\!\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_{\!y}$$



The resulting products were reprecipitated several times to remove unreacted monomers. The number average molar masses are presented in Table 1.

Aromatic polymethacrylates exhibit intensive absorption bands in the ultraviolet spectrum. These are $\pi-\pi^{x}$ transitions at wavelengths less than 250 nm and $n-\pi^{x}$ transitions at higher wavelengths. In the case of poly(phenyl methacrylate) the $n-\pi^{x}$ transition is located at 260 nm.

The introduction of substituents in the phenolic nucleus results in a red shift of the absorption band /5/, which is influenced by the type and position of the substituent. Accordingly, poly(chlorophenyl methacrylates) exhibit different absorption regions, depending on the position of the chlorine in the phenolic nucleus. Poly(2-chlorophenyl methacrylate) and poly(3-chlorophenyl methacrylate) show $n-\pi^{x}$ transitions at 266 and 273 nm, see Figure 1.

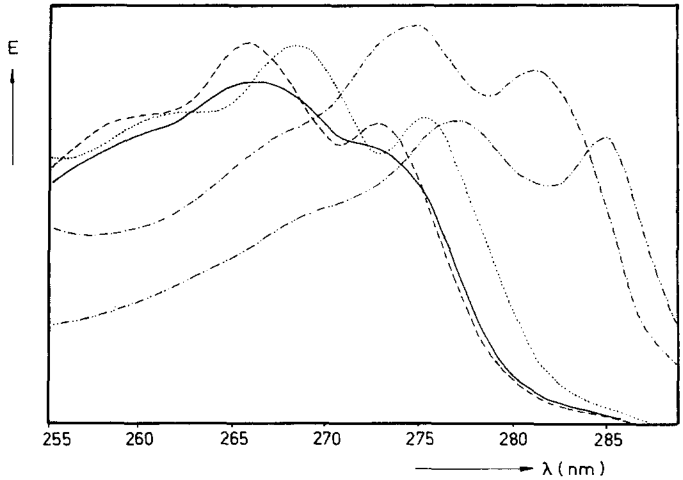
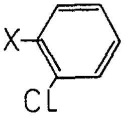
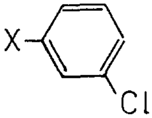
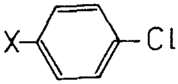
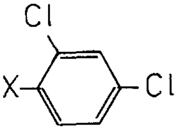
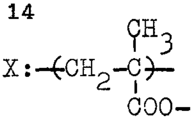
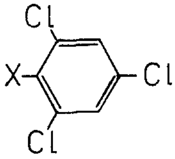


Figure 1: Absorption spectra of poly(chlorophenyl methacrylates) in tetrahydrofuran; poly(2-ClPh-MA)(____), poly(3-ClPh-MA)(- - -), poly(4-ClPh-MA)(....), poly(2,4-ClPh-MA)(-.-.-), poly(2,4,6-ClPh-MA)(-..-..-)

The substitution in para-position results in the appearance of the appropriate bands at 269 and 275 nm. An even more pronounced red shift is obtained for dichloro and trichloro substituted compounds, i.e. poly(2,4-dichlorophenyl methacrylate) at 275 nm and 282 nm and poly(2,4,6-trichlorophenyl methacrylate) at 277 nm and 286 nm.

The absorption maxima and the corresponding extinction coefficients of the poly(chlorophenyl methacrylates) are presented in Table 2.

Table 2: Weight Related (ε^x) an Molar Extinction Coefficients of the Poly(chlorophenyl methacrylates)

Sample	Structure	λ (nm)	ε^x (l/g x cm)	ε (l/mole x cm)
1		266 273	1,82 1,46	356 287
4		266 273	1,73 1,40	339 274
7		269 275	2,26 1,82	443 357
10		275 282	2,59 2,41	596 554
14  $X: -(CH_2-\underset{COO-}{\overset{CH_3}{C}})-$		277 286	1,50 1,42	396 375

U.V. spectra of different concentrations of the chlorophenyl methacrylate homopolymers were taken and graphs were plotted of absorbance value at the lower absorption maximum vs. concentration, see Figure 2.

For all homopolymers linear relationships were obtained, indicating that Lambert-Beer´s law was valid in the appropriate concentration range.

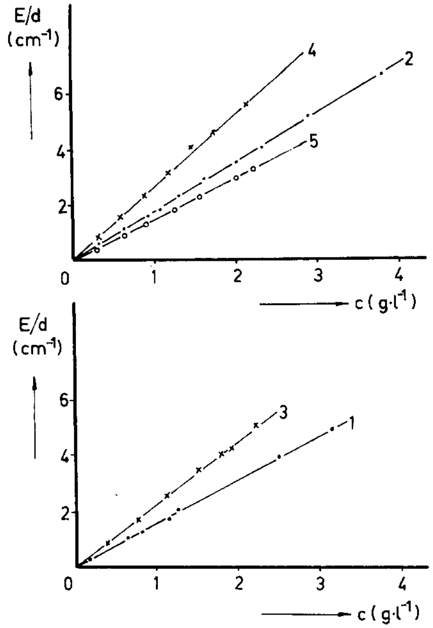


Figure 2: Absorbance vs. concentration of poly(chlorophenyl methacrylate); (1)- 2-ClPhMA, (2)- 3-ClPhMA, (3)- 4-ClPhMA, (4)- 2,4-ClPhMA, (5)- 2,4,6-ClPhMA

Assuming that the absorption of PMMA at wavelengths higher than 260 nm is very low (< 5 l/mole cm) it was expected, that the absorption behaviour of the chlorophenyl methacrylate-MMA-copolymers at $\lambda \geq 260$ nm is only influenced by the chlorophenyl methacrylate moiety. In this case the copolymer composition could be directly determined from the intensity of the appropriate absorption bands in this wavelength region. Furthermore, it was assumed that the absorption behaviour of the copolymers can be simulated using mixtures of the homopolymers, i.e. poly(chlorophenyl methacrylate) and PMMA.

Figure 3 shows the weight related extinction coefficient vs. concentration of mixtures of different poly(chlorophenyl methacrylates) and PMMA. In all cases linear dependences were obtained, indicating that using these calibration curves the composition of any mixture can be determined measuring of the appropriate sample.

In order to evaluate, if the calibration curves can be used for the analysis of copolymers as well, a number of 4-chlorophenyl methacrylate-MMA-copolymers was measured by U.V. spectroscopy and their was calculated. Figure 4 demonstrates that for copolymers of different composition similar U.V. spectra are obtained.

From the appropriate calibration curve the concentration of the 4-chlorophenyl methacrylate units was determined. The results are summarized in Table 3 and compared with data from the chlorine analysis.

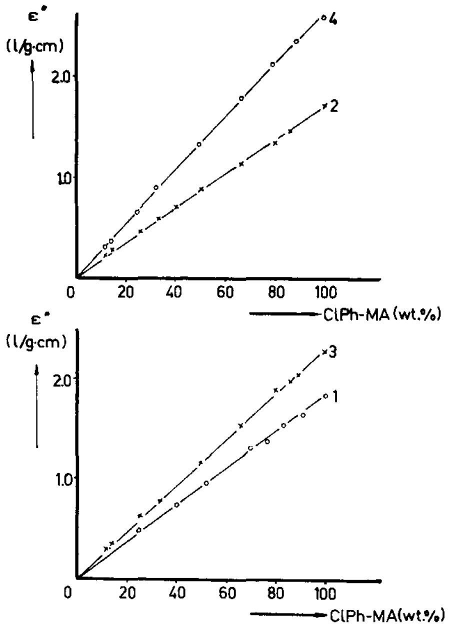


Figure 3: Weight related extinction coefficient vs. concentration of poly-(chlorophenyl methacrylate) in mixtures with PMMA; (1)- 2-ClPhMA, (2) - 3-ClPhMA, (3)- 4-ClPhMA, (4)- 2,4-ClPhMA

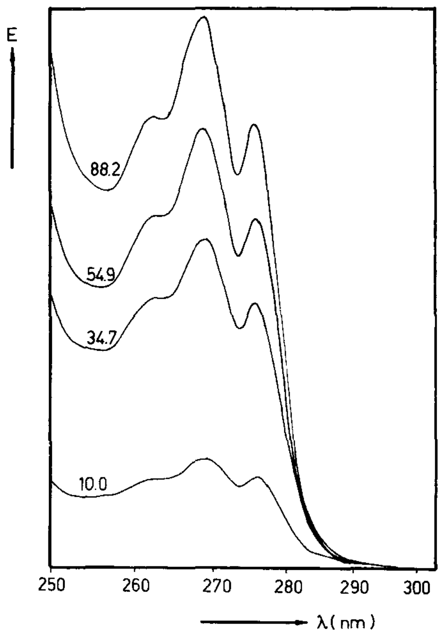


Figure 4: Absorption spectra of 4-chlorophenyl methacrylate copolymers of different composition (mole%), concentration 2,45 g/l

Table 3: Compositional Analysis of 4-Chlorophenyl Methacrylate-MMA-Copolymers

Polymer	Concentration of 4-ClPhMA			
	Monomer Mixture	U.V.		Cl-Analysis
	(mole%)	(wt.%)	(mole%)	(mole%)
15	5,0	9,3	5,0	5,3
16	10,0	17,9	10,0	10,2
17	20,0	43,1	27,9	27,9
9	25,0	48,3	32,3	33,1
18	30,0	51,0	34,7	33,7
19	40,0	57,4	40,7	41,0
20	50,0	70,5	54,9	54,9
8	50,0	74,4	59,7	58,4
21	60,0	75,0	60,5	59,6
22	96,0	98,7	97,5	96,7

Table 4: U.V. Spectroscopical Determination of the Copolymer Composition Compared to the Chlorine Analysis

Polymer	Concentration of ClPhMA			
	Monomer Mixture	U.V.		Cl-Analysis
	(mole%)	(wt%)	(mole%)	(mole%)
2	50 2-ClPhMA	69,6	53,8	53,3
3	50 2-ClPhMA	65,9	49,7	45,1
5	50 3-ClPhMA	69,3	53,5	53,3
6	41 3-ClPhMA	59,5	42,8	41,9
11	50 2,4-ClPhMA	76,7	58,9	57,7
12	28 2,4-ClPhMA	48,8	29,2	29,4
13	18 2,4-ClPhMA	36,8	20,1	19,0

In all cases an excellent agreement of both methods was obtained.
In Table 4 the compositional analysis of other chlorophenyl methacrylate copolymers is presented. Again the agreement of U.V. spectroscopy and chlorine analysis is very good.

CONCLUSIONS

A rapid method based on U.V. spectroscopy for the analysis of chlorophenyl methacrylate-MMA-copolymers has been developed. It has been demonstrated that the copolymer composition can be determined using calibration curves based on mixtures of the corresponding poly(chlorophenyl methacrylate) and PMMA. A comparison with results of the chlorine analysis show that both methods are equally suited for the copolymer analysis.

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