PREPARATION OF GRAFT COPOLYMERS BY THE REACTION OF POLYMERIC ACYL CHLORIDES WITH MONOHYDROXY-TERMINATED POLYMERS: AN INTRODUCTORY STUDY

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Dedicated to the memory of Dr K. Bláha.

An attempt was made to prepare well-defined graft copolymers by the coupling reaction between acyl chloride groups located along the backbone chain and monohydroxy-terminated grafts prepared separately. The molecular weights and the parameters of heterogeneity in chemical composition of the products were determined by light scattering and osmometry. The determination of molecular characteristics revealed that the degree of grafting was low. The results therefore could not be confronted with a statistical model at this stage. The problems encountered in the synthesis, e.g., gel formation, and the data relating to the soluble products are discussed.

Graft copolymers are of great and increasing industrial importance, and are also of permanent scientific interest. Even though a vast literature exists on their synthesis, the reported characterization has rarely been sufficiently rigorous to establish that the structure expected from the assumed chemistry of synthesis is actually achieved in reality.

There are three basic methods for graft copolymer synthesis: (i) grafting onto a backbone, when polymer grafts are attached to a preformed polymer backbone, (ii) grafting from a backbone, when grafts are formed by polymerization from initiation sites located on the backbone, and (iii) the macromonomer technique[1], when the backbone is formed during the copolymerization of a low-molecular-weight monomer with a macromonomer.

The purpose of this paper is to discuss the feasibility, advantages, and problems of the various methods for the preparation of graft copolymers, especially in relation to the characterization of their molecular structure. The reaction between methacryloyl

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chloride units (MAC) located in the backbone with monohydroxy-terminated poly-mers, has been chosen. As a backbone, either poly(methacryloyl chloride) (PMAC) or the azeotropic copolymer of styrene (S) with MAC has been used. The latter is virtu-ally an alternating copolymer, poly(S-*alt*-MAC), because both monomer reactivity ratios are low[2], viz., $r_S = 0.13$, $r_{MAC} = 0.075$. This particular copolymer was selected for the grafting studies, because Polowiński[3] reported enhanced reactivity of MAC units towards hydroxy compounds when the chain contains styrene units.

After completion of the grafting reaction, residual acyl chloride groups in poly-(S-*alt*-MAC) can be converted to ester units by reaction with, e.g., methanol[3]. The final products are graft copolymers with poly(S-*alt*-methyl methacrylate) back-bones and the chosen grafts. Such copolymers without reactive acyl groups are more suited for the subsequent characterization of the molecular structure, which is the principal objective of this study.

Monohydroxy-terminated samples of poly(oxyethylene) (POE-OH), poly(di-methylsiloxane) (PDMS-OH), and poly(methyl methacrylate) (PMMA-OH) were used as grafting agents. The selection of these particular components was based on some results reported in the literature:

Gramain and Frère[4,5] prepared poly(acryloyl chloride) and, during grafting with POE-OH, observed unexpected self-gelling of the products. De Vos and Goethals[6] recently found that the commercial monohydroxy-terminated POE-OH contained a portion of molecules having hydroxy groups at both ends of the chian; these, inevitably, are expected to function as a cross-linking agent. It is one of the objectives of this study to check the grafting reaction with this type of functional polymer.

Recently, Smith and McGrath[7,8] prepared poly(methyl methacrylate) (PMMA) grafted with PDMS by copolymerization of methyl methacrylate with a macro-monomer, and the present study offers an alternative approach to the synthesis.

Finally, the lately-developed group-transfer-polymerization[9-11] (GTP) facilitates the preparation of monohydroxy-terminated polymethacrylates, which are con-venient subjects for studies of grafting.

EXPERIMENTAL

Chemicals

Styrene (Lachema, Czechoslovakia) was washed with a 2% aqueous solution of sodium hydroxide, dried with anhydrous magnesium sulphate followed by calcium hydride, and distilled on a labora-tory column under reduced pressure. Methacryloyl chloride (Fluka AG, Switzerland) was freshly distilled before the copolymerization experiment. The content of methacrylic acid was about 0·2 wt. %. 2,2'-Azobis(isobutyronitrile) (AIBN, BDH Chemicals Ltd., U.K.) was re-crystallized twice from methanol. Methanol was dried over calcium hydride and distilled before use. Benzene was dried by treatment with solid sodium hydroxide, followed by azeotropic distilla-

tion. Other solvents and materials used in the characterization of polymers were of analytical reagent grade, and were distilled before use. The purity ($<99\%$) was checked by gas chromatography.

Backbone

In a typical experiment, MAC (20 g, 0·192 mol) or a mixture of MAC (10 g, 0·096 mol) and styrene (10 g, 0·096 mol) was mixed with dry benzene (20 cm^3); AIBN (300 mg, i.e., 4·6 . . 10^{-2} mol l^{-1}) was added. Radical copolymerization was allowed to proceed under an inert nitrogen atmosphere at 60°C for 24 h. The viscous solution was diluted with dry benzene; the concentration of polymer was about 33 wt. %. Some of the solution was precipitated into dry cyclohexane to determine the conversion (95—96 wt. %), molecular weight, chemical composition of the backbone (51 wt. % of styrene in the case of the copolymer) and the time needed for complete methanolysis.

Methanolysis of the Backbone

To three parts of a benzene solution of the backbone, one volume part of methanol was added. Infra-red spectra and elemental analysis of the chlorine content showed that methanolysis of the backbone needs about four days to complete the conversion ($>99\%$) of acyl chloride into ester groups. Before methanolysis, the isolated backbone was not soluble in common solvents, a result attributed to the formation of anhydride bonds due to the presence of a trace amount of methacrylic acid in the methacryloyl chloride. Treatment by methanol destroys the cross-links by formation of ester groups.

The mean molecular weights of the methanolysed backbone, poly(S-*alt*-MMA) were found to be 38 000 (M_n, by membrane osmometry) and 75 000 (M_w, by light scattering).

Grafts

POE-OH was a commercial product of Aldrich Chemical Co., U.S.A., labelled $M_w = 5\,000$, m.p. 59°C. The polymer was dissolved in benzene (80 vol. %)–pyridine mixture. Traces of moisture were removed by azeotropic distillation. A 17·6 wt. % solution of POE-OH was used in the subsequent experiments.

PDMS-OH was kindly prepared by Dr. S. J. Clarson, University of Cincinnati, U.S.A., by anionic polymerization of hexamethylcyclotrisiloxane (Petrarch Systems Inc., U.S.A.) in dry toluene with tert-butyllithium. Living anions were terminated by addition of water. Molecular weights were determined by vapour-pressure osmometry ($M_n = 6\,300$) and by light scattering ($M_w = 9\,400$). Water was removed by azeotropic distillation with benzene (80 vol. %)–pyridine mixture. The final concentration of polymer in the solution was 19·6 wt. %.

PMMA-OH was a product of group-transfer polymerization (GTP). The method was described previously[9−11] and applied especially to acrylates and methacrylates. In our case[12], a more complex procedure was used to prepare the GTP initiator[9], [2-methyl-1-(2-trimethylsiloxyethoxy)-1-propenyloxy]trimethylsilane. As a catalyst, the hydrogen bifluoride anion was used. After termination of methyl methacrylate polymerization with water, PMMA-OH was obtained. The same procedure for drying as above was used; a 9·5 wt. % solution of PMMA-OH in benzene (80 vol. %)–pyridine mixture was used in the grafting experiments. Molecular weights of PMMA-OH were 80 000 (M_n, by membrane osmometry) and 126 000 (M_w, by light scattering).

Synthesis of Graft Copolymers

The dry benzene solutions of the backbone and potential grafts were mixed so that the resulting ratio backbone/grafts would be approximately 1/1 by weight (in case of PDMS grafts, other proportions were also chosen). The reaction mixtures were shaken for 7 days at 25°C. In some cases (POE-OH, PDSM-OH) the miscibility of the solutions was limited, and two liquid phases coexisted. Moreover, after 1—3 days gel formation was observed.

Methanol was then added up to 25 vol. %, and the samples were shaken for another 4—7 days at room temperature to complete conversion of the residual acyl chloride groups into methyl methacrylate units. Polymers were precipitated by pouring the solutions into an excess of methanol (each phase separately, if more than one liquid phase was present) and dried over phosphorus pentoxide in vacuo. Recovery of the material was close to 100% in all cases.

Methods of Characterization

Number-average molecular weights, M_n, were determined in toluene solution with a membrane osmometer Wescan, model 230, or vapour-pressure osmometer Hitachi Perkin Elmer, model 115, in methyl tert-butyl ether.

Weight-average molecular weights were evaluated from light-scattering measurements in various solvents with either a Sofica 42·000 or FICA 50 apparatus (546 nm, 25°C). Solutions for measurement were optically clarified by filtration through a sintered-glass filter G5 (VEB Jenaer Glaswerke, G.D.R., average porosity c. 1 μm). Refractive index increments were taken from the literature[13] or measured with a Brice–Phoenix differential refractometer BP-2000-V (546 nm 25°C).

The chemical compositions of all the polymer materials were determined by elemental analysis.

For fractionation between two demixing liquids[14,15] the pair of solvents, tetrachloroethylene (TCE) and dimethyl sulfoxide (DMSO) was selected[16]; the critical temperature is 56°C at 85 vol. % of TCE. The upper, DMSO-rich, phase dissolves the more polar part of the reaction product, while in the TCE-rich phase the other part is soluble. After dissolution of the reaction product in this solvent mixture at elevated temperature (60°C), the system was cooled down, and typically three phases were formed when equilibrium was reached at 25°C. Material collected from each phase was characterized by its chemical composition and molecular weight.

RESULTS AND DISCUSSION

Grafting with POE-OH

The reaction of a backbone polymer with POE-OH led in all cases to crosslinked products, regardless of the backbone type, i.e., with both PMAC and poly(S-*alt*--MAC). The presence of a substantial gel fraction was observed. This result resembles the situation described by Gramain and Frère[4,5], who reported the formation of "self-gelling polymers" in the reaction of polyacryloyl chlorides with POE-OH; they attributed the occurence of the gel to the presence of stereocomplexes formed by interaction between grafts.

In the POE-OH manufactured by Aldrich Chemical Co., used in the present study, 20% of the molecules are dihydroxyterminated[6]. The POE-OH from Polysciences

Ltd., used by Gramain and Frère[4,5], contains up to 25% molecules with hydroxy groups at both ends[6]. Generally, commercial PEO-OH samples contain a larger fraction of dihydroxy-terminated molecules the higher is their molecular weight.

Thus, under the present conditions, the grafting reaction must be expected always to be accompanied by crosslinking. Consequently, this type of synthesis is not convenient for preparation of completely soluble graft copolymers, unless perfectly monohydroxy-terminated poly(oxyethylene) is available.

The same conclusion is valid for the synthesis of macromonomers from mono-hydroxy-terminated POE-OH by acylation with methacryloyl chloride. The presence of dihydroxy-terminated POE molecules gives rise to bifunctional macromonomer molecules. When copolymerized with an ordinary monomer, branched and cross--linked structures are expected to result; such structures were indeed observed[4].

Grafting with PDMS-OH

Several grafting experiments with PDMS-OH provided rather conflicting results. The reaction products consisted of two coexiting liquid phases. One of them contained the graft copolymer (and some gel in one case), the other ungrafted PDMS--OH, which was thus easy to separate. Most of the original PDMS-OH was recovered after the reaction (Table I), which indicates a low efficiency of grafting. Because of the gel formation, it may seriously be doubted, that each PDMS-OH molecule indeed contains a single terminal hydroxy group. An alternative explanation for the gel formation may be the presence of the product of hydrolysis of hexamethylcyclo-

TABLE I

Analysis of the reaction mixture and the apparent molecular weights, M_{ap}, in the grafting of PDMS-OH to poly(S-*alt*-MAC)

Starting mixture of polymers, wt. % of PDMS-OH	Reaction mixture, wt. %			$M_{ap} \cdot 10^{-3}$	
	unreacted PDMS-OH	soluble copolymer	copolymer gel	after methanolysis[a]	in chloroform[b]
0	—	—	—	80	75
25	24	76	—	70	80
50	35	65	—	965	105
75	41	15	44	∞	160

[a] After 4 days in methanol (25 vol. %)–benzene. Light scattering from methyl ethyl ketone solutions was measured. [b] The molecular weight was determined by light scattering in chloroform after 4 days standing.

trisiloxane, the starting material for PDMS-OH synthesis, which, having two hydroxy groups in one molecule, would act as a cross-linking agent.

It is difficult to specify the nature of the cross-links, the gel was found to dissolve completely in chloroform within several days, moreover the soluble samples were observed to decrease in molecular weight in this solvent (Table I). Only apparent molecular weights (cf. below) were determined.

In close proximity to the point where a graft is joined to the backbone, the side-chain contains a C—O—Si link. Such groups (in contrast to Si—O—Si) are susceptible to solvolytic cleavage, for example by water or alcohols. It is difficult to be certain that water is totally absent from the system and, since chloroform contains 1% of ethanol as a stabilizer, one cannot rule out some transesterification with consequent detachment of grafts from the backbone. In the case of gels this process would decrease the degree of cross-linking and might render the polymer soluble.

More detailed characterization has been abandoned since the chemistry of gel formation and the behaviour in chloroform are not completely understood.

For the separation of homopolymers from the true graft copolymer, phase equilibria in demixing liquids[14,15] were established. Separation is then achieved in a single step. The method can also be applied for the fractionation of graft copolymers according to chemical composition, if the phase equilibrium is established repeatedly at gradually rising temperature[15,16].

A fractionation experiment with one of the products revealed very low contents of grafts in all fractions (Table II). Several backbones seem to be connected together (cf. the hydrolyzed hexamethylcyclotrisiloxane cross-link hypothesis mentioned

TABLE II

Fractionation of poly(S-*alt*-MMA)-*graft*-PDMS in demixing solvents DMSO–TCE; 50 wt. % of PDMS-OH in the starting mixture, cf. Table I. Symbols: T is the temperature, w is the weight fraction of polymeric material isolated in a particular fractionation step from the specified phase, with respect to the total amount of polymeric material fractionated, M_w is the weight-average molecular weight, x is the composition of the fraction, expressed in terms of the weight fraction of the backbone component

Fractionation step	T °C	Number of phases	DMSO-rich phase			TCE-rich phase		
			w	$M_w \cdot 10^{-3}$	x	w	$M_w \cdot 10^{-3}$	x
1	22	3	0·098	120	1·03	0·146	100	0·67
2	31	3	0·132	330	1·02	0·060	270	0·84
3	36	3	0·072	510	0·99	0·082	280	0·97
4	42	3	0·078	610	1·02	0·092	340	0·99
5	45	2	0·229	2 630	1·00	0·011	1 560	0·83

above), because the molecular weight of the backbone-rich fractions (Table II) is always much higher compared to that of the ungrafted backbone prior to use in the grafting experiments (Table I).

Grafting with PMMA-OH

The most successful result, as far as the solubility of the products is concerned, was the synthesis of poly(S-*alt*-MMA)-*graft*-PMMA, using PMMA-OH prepared by the GTP procedure as the grafting agent.

The product isolated after reaction was characterized by the light scattering method, which is an effective tool for the investigation of copolymers on the molecular level. With chemically heterogeneous copolymers, light scattering yields, instead of the weight-average molecular weight, M_w, only apparent values, M_{ap}, which depend on the refractive index of the solvent or on related quantities[17,18]. According to Bushuk and Benoit[17], this dependence can be described by a quadratic equation,

$$M_{ap} = M_w + 2PR + QR^2 ,\qquad(1)$$

where $R = \Delta v/v$; Δv is the difference between the refractive index increments of the backbone and grafts in a given solvent; v is the refractive index increment of the copolymer in the same solvent. The experimental determination of M_{ap} in at least three solvents with sufficiently different refractive indices makes it possible, using Eq. (1), to find the true weight-average molecular weight M_w, and the parameters of the chemical heterogeneity[17,18] P and Q.

The apparent molecular weights of the reaction product have been determined in several solvents (Table III). The least-squares fit of the parabola according to

TABLE III

Apparent molecular weights, M_{ap}, obtained by light scattering from solutions of poly(S-*alt*-MMA) -*graft*-PMMA in various solvents

Solvent	$R = \Delta v/v$	$M_{ap} \cdot 10^{-3}$
Methyl ethyl ketone	0·39	290
Tetrahydrofuran	0·50	370
1-Bromonaphthalene (42·5 vol. %)–methyl ethyl ketone[a]	2·01	660
1-Bromonaphthalene (80 vol. %)–methyl ethyl ketone[b]	−0·68	140
1,2,4-Trichlorobenzene	−1·26	100

[a,b] Mixed solvents, isorefractive[21] with [a] PS and [b] PMMA; the refractive index increments were determined at osmotic equilibrium between the solution and mixed solvent.

Eq. (1) yields $M_w = 251\,000$, $2P = 157\,000$, and $Q = 24\,000$. In Fig. 1, the parabolic graph for the reaction product is compared with that constructed for a hypothetical mixture of nonreacted backbones and grafts having the same overall chemical composition as the graft copolymer. It is obvious that the two parabolas differ substantially, thus providing evidence that the reaction product is not a simple mixture of backbones and grafts, i.e., that grafting had taken place. Moreover, the true molecular weight of the grafted product, $M_w = 251\,000$, is higher than that of the unreacted backbones, $M_w = 75\,000$, or the unreacted grafts, $M_w = 126\,000$.

The average number of grafts, m_n, in a copolymer macromolecule is defined as a ratio of the number-average molecular weight, M_n^G, of the total grafts to that,

TABLE IV

Separation of the reaction product of poly(S-*alt*-MMA)-*graft*-PMMA synthesis in the demixing solvents DMSO–TCE at 25°C. w is the weight fraction of the material from the total amount obtained after fractionation; only 70 wt. % of starting material (a copolymer isolated from the reaction mixture) was recovered

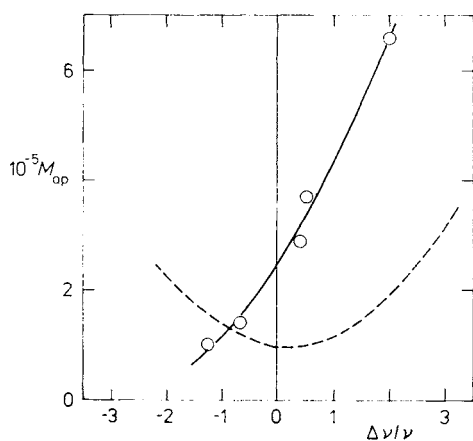| Phase	w	Backbone content, wt. %
Upper, DMSO-rich	0·37	35
Middle	0·59	88
Lower, TCE-rich	0·04	95

FIG. 1

Dependence of the apparent molecular weights, M_{ap}, of the product of grafting PMMA-OH to poly(S-*alt*-MAC) backbone on the optical parameter $\Delta v/v$ (open circles and full line), and a comparative plot expected for a mixture of backbones and grafts with the same composition (broken line)

M_n^*, of individual grafts,

$$m_n = \frac{M_n^G}{M_n^*} = \frac{(1 - \bar{x}) M_n}{M_n^*} . \tag{2}$$

The former can be expressed by means of the number-average molecular weight of the whole copolymer, $M_n = 70\,000$, and the average chemical composition, $\bar{x} = 0.50$ (weight fraction of the backbone). If we assume that no PMMA-OH is present as homopolymer and that its $M_n^* = 80\,000$, we obtain $m_n = 0.44$. The fact that $m_n < 1$ indicates a very low degree of grafting and also the presence of ungrafted backbones. This result is partly a consequence of the high molecular weight of the PMMA-OH. Because of the very low concentration of terminal hydroxy groups, the number of grafts can never be high.

In a simple separation experiment in demixing solvents, the pure ungrafted backbones and unattached grafts were not detected. However, the material from the middle and the lower phases consists essentially of backbones (Table IV). The upper phase seems to contain the main portion of the graft copolymer.

CONCLUSIONS

Grafting of monohydroxy-terminated polymers to backbones carrying acyl chloride groups cannot be regarded as successful with POE-OH and PDMS-OH. The basic problem resides in the difficulty of preparing polymers with exclusively one hydroxy end-group, in order to avoid the subsequent formation of cross-linked structures. Another difficulty encountered in the synthesis is the limited miscibility of solutions of backbones and grafts, which unfavourably influences the extent of grafting.

Grafting of PMMA-OH prepared by GTP to poly(S-alt-MAC) backbones seems to be the most promising of the methods explored. The reaction was homogeneous, a soluble product was formed, no gel was observed. There is a substantial difference between the Bushuk–Benoit parabola for the grafted product and that for a mixture of backbones and grafts. This result indicates that grafting does take place.

It would be helpful, if a product having more grafts with lower molecular weight could be prepared. The possibilities of the GTP method may be rather limited here, for the reaction does not work properly when a larger amount of initiator is used. Experiments concerning the preparation of PMMA-OH with a lower molecular weight, comparable to that of our POE-OH or PDMS-OH, are in progress.

The original intention to confront the experimentally determined characteristics of well-defined graft copolymers with the predictions of model calculations[19,20] turned out, unfortunately, not to be feasible with the materials available at the present time, but the difficulties are largely understood and are likely to be overcome in the near future.

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