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Free radical grafting onto cellulose in homogeneous conditions. 2. Modified cellulose–methyl methacrylate system

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Abstract

The homogeneous grafting of methyl methacrylate (MMA) onto methacrylate-modified cellulose (CEMA) was achieved by a two-step process at three different temperatures (T_p) in the range 40–70°C. Grafting yield (GP%) and grafting efficiency (GE%) were determined and related to the conditions of synthesis. The role of various reaction parameters on GP% and GE% (namely, reaction temperature and time, cellulose degree of substitution (DS), molar ratios of MMA to methacrylate pendant groups (–MA) and of MMA to initiator) was evaluated. Molecular weights of grafted chains and of PMMA homopolymer were determined at the chosen T_p and compared to each other. The average number of grafts per cellulose molecule (n_g) was calculated and, together with the molecular weight data of the grafted chains, utilized to interpret the experimental trend of GP% vs. T_p. On the basis of the above results, interesting perspectives of the homogeneous grafting method were outlined. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Grafting yield; Methyl methacrylate; Homopolymer; Grafting efficiency

1. Introduction

Cellulose (CE) grafting is a process aimed at introducing some branches of synthetic polymers into the main polysaccharide chain in order to confer specific additional properties to the cellulose itself, without destroying its intrinsic characteristics. A few examples may be useful to specify the above objective—(i) tensile strength and abrasion resistance, shown by cotton fabrics, are considerably improved by 27% (w/w) acrylonitrile (AN) grafting (Demint, Arthur Jr. & McSherry, 1961); (ii) excellent thermoplasticity and water absorption are observed for cotton grafted with ≥ 40% (w/w) styrene (Sakurada, 1962; Sakurada, Okada & Kaji, 1972). In particular, tensile properties of single cellulosic fibre remain almost unaltered after styrene grafting via γ-irradiation. The tendency to water absorption calculated on the basis of cellulose content, despite the increased hydrophobicity, increases on increasing the percentage of graft. (iii) In other cases, i.e. for fabrics grafted with vinyl acetate and AN (Blouin, Morris & Arthur Jr., 1966), a moderate increase in tear and tensile strength together with an exceptionally high degree of abrasion resistance is observed.

In spite of the lack of comprehensive review on the subject, it is now clear that the approach to reach optimum grafting is linked to the desired property. For instance, internal grafting is necessary when the dyeing behaviour of fibres has to be changed, while surface grafting is sufficient to just improve the abrasion resistance. In this regard, many interrelated problems need to be faced and solved—how to control the extent of grafting and minimize the homopolymer formation, which is always present in the grafting process; how to control the graft number and distribution; how to determine the graft molecular weight and how this compares with the homopolymer molecular weight; how to ensure product homogeneity, and so on. In our opinion, the entire set of answers to the above questions may only be given on the basis of new processes developed in homogeneous conditions, processes which became possible only in recent years following the discovery of undegrading solvents of cellulose (Turbak, El-Kafrawky, Snyder & Auerbach, 1982; Hudson & Cuculo, 1980).

Instead, the grafting onto CE is still based on a heterogeneous reaction in which both the state of aggregation and the physical structure of cellulose play an important role, inasmuch as the grafting proceeds through radical formation on the undissolved cellulose where the unsaturated monomer polymerizes. Obviously, in these conditions the system

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is chemically quite complex, and polymerization temperature and time act as relevant reaction parameters. In general, it has been demonstrated (Hebeish & Mehta, 1967) that the CE accessibility strongly affects both the fine structure of the final product and the total yield. When the grafting process mainly involves the fibre surface, the number of grafted chains per cellulose molecule is in the range of unity (0.2/2) and the molecular weight of the side chains may be of the order of 10^5. The situation is quite different when polymerization occurs inside the fibres, where the homopolymer remains entrapped with a noticeable increase in volume. Typically, the CE conversion is estimated to be only 20–30% of the initial CE weight, reaching values up to 70–80% only when the amount of grafted polymer is very high (200–500% of the initial CE weight). Consequently, the products contain both the copolymer and the unchanged CE to a greater or lesser extent (Rogovin, 1972). The advantages of the synthesis performed in homogeneous conditions have been underlined by several authors in the case of CE derivatives (Diamantoglou & Kundinger, 1995). Results on the DS control, and on the uniform distribution of substituents along the CE chain, and optimization of the reactant yield are reported by Diamantoglou and Kundinger (1995). However, concerning the copolymer synthesis from underivatized CE, there are rather limited studies despite the actual knowledge of undegrading CE solvents. Among these, the suitability of dimethylacetamide (DMAc)/lithium chloride and *N*-methylpyrrolidone (NMP)/lithium chloride is particularly evident, considering the fact that the cellulose chains do not change or lose their characteristic rigidity during the solution process.

A recent paper by our research group (Bianchi, Marsano, Ricco & Russo, 1998) describes the homogeneous synthesis of CE-g-AN copolymers, obtained by means of a two-step process: CE, dissolved in dimethylacetamide (DMAc) containing 5% (w/w) of LiCl, is treated with a suitable amount of acryloyl chloride, thus obtaining a cellulose derivative characterized by the presence of some pendant double bonds. Subsequently, AN is added and grafted onto the unsaturated groups by free radical copolymerization initiated by azobisisobutyronitrile (AIBN). The amount of grafted polyacrylonitrile with respect to cellulose varies between 17 and 190% (w/w) by suitable control of the reaction parameters (reactant ratio, reaction time and temperature). It can be estimated that the average value of the degree of polymerization for the branched chains is about seven.

In the present paper, results of the grafting reaction of MMA onto the modified cellulose are given. The need for monomers to be homogeneously grafted onto CEMA is linked to the specific properties that we would like to confer to the system. In this regard, MMA represents a suitable choice as its homopolymer is characterized by high T_g, no crystallinity, excellent optical properties, etc. and offers a wide opportunity for alternative or additional application, as compared to AN.

2. Experimental

2.1. Materials

CE: The sample of regenerated CE (degree of polymerization 260) was supplied by ‘Stazione Sperimentale cellulosa, carta e Fibre Tessili vegetali ed Artificiali’ (Milan, Italy). The samples were submitted to double extraction with water and petroleum ether, followed by oven drying at 50°C for 7 days under vacuum (Bianchi et al., 1998) before use. A mother solution of CE in DMAc/5% LiCl at the polymer concentration $C_p = 4\%$ (w/w), was prepared according to Turback’ procedure (Turback, El-Kafrawky & Auerbach, 1981).

DMAc: Supplied by Fluka; it was distilled under vacuum on CaH_2 and stored on molecular sieves in nitrogen atmosphere.

MACl: Supplied by Fluka; it was stored at low temperature in nitrogen.

MMA: Supplied by Fluka at a purity degree of 99% (hydroquinone as polymerization inhibitor), it was washed with an aqueous solution of NaOH and deionized water, and stored at low temperature in nitrogen in the presence of anhydrous Na_2SO_4.

LiCl (98%), AIBN (98%), Na_2SO_4 (99%), NaOH pellets, H_2SO_4 (96%), ethanol (96%), diethyl ether (98%), methanol (99%), dioxane (98%), acetone (99%), benzene (99%), *N,N*-dimethylformamide were supplied by Fluka and used without further purification.

CaH_2 (94%) and molecular sieves (4 Å type) were supplied by Riedel-de-Haen.

2.2. Procedure

Compared to our previous work (Bianchi et al., 1998), the only major difference lies on the choice of the acyl chloride used for the modification of cellulose. Instead of acryloyl chloride, methacryloyl chloride (MACl) was selected for a better matching with MMA repeat units. An aliquot of the solution containing about 1 ÷ 1.5 g of CE at $C_p \sim 2.5\%$ was obtained by DMAc dilution of the mother solution. After thermostating at a fixed temperature, MACl diluted with DMAc was added dropwise to the above solution under anhydrous conditions and left to react for 2.5 h. A portion of the mixture was then taken to determine the degree of substitution (DS) defined by the following relation:

$$\mathrm{DS} = (W_{\mathrm{CEMA}} - W_{\mathrm{CE}})/(m_{\mathrm{A}} - 1)n_{\mathrm{CEu}}, \qquad (1)$$

where W_{CE} and W_{CEMA} are the weights of the sample before and after derivatization, respectively, m_{A} is the molecular weight of the acyl residue and n_{CEu} are the moles of CE repeat units. W_{CEMA} was obtained by diethylether precipitation, followed by washing with hot water and oven drying in vacuum at 50°C for 24 h. The remaining aliquot of CEMA was used to synthesize the graft copolymer after stripping both the unreacted acyl chloride and the produced HCl by

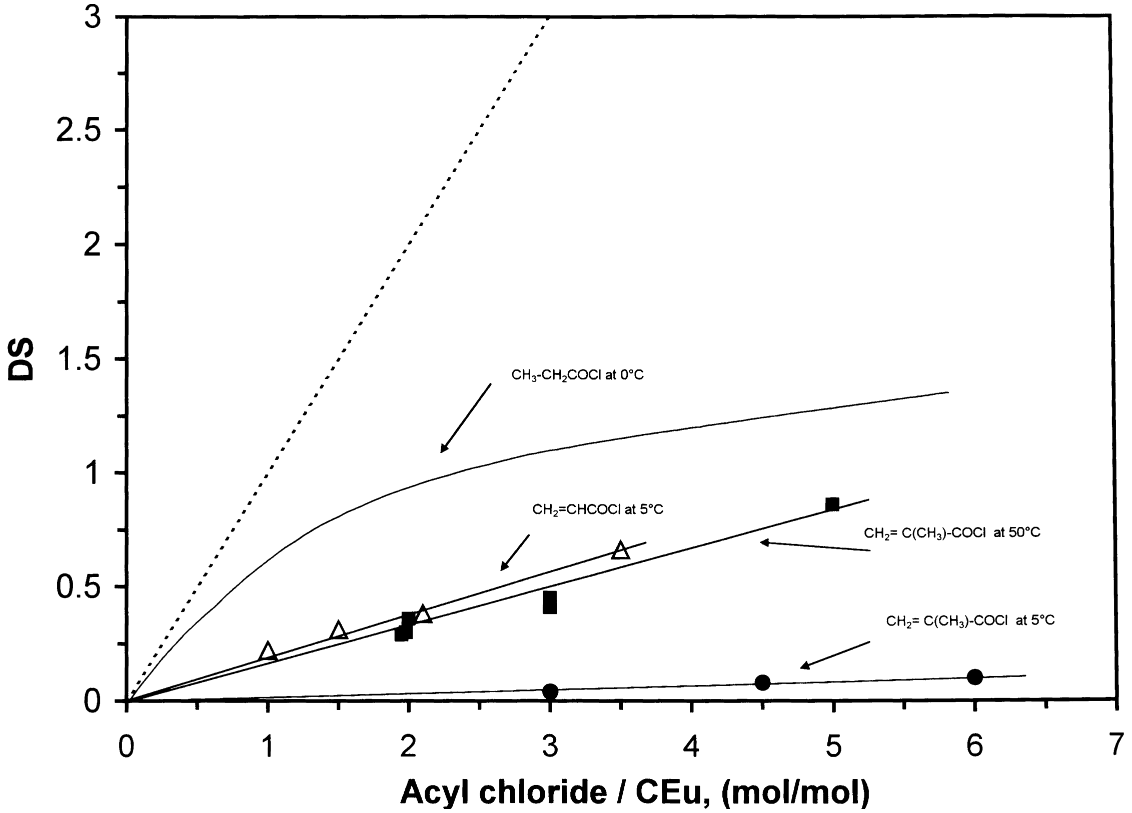


Fig. 1. Substitution degree (DS) of derivatized cellulose vs. acyl chloride/glucosidic unit of CE molar ratio.

bubbling nitrogen in solution. The mixture was left to react for a specific time (t_p), which was for example 6 h at 60°C for the first set of experiments. Various CE-g-PMMA samples were prepared in such a way. The amount of formed homopolymer was evaluated after Soxhlet extraction with dioxane for 2 h.

2.3. Characterization methods

Viscometry: The intrinsic viscosity, $[\eta]$, of PMMA was determined in benzene by using a suspended-level Ubbelhode viscometer (solvent flow time > 100 s) in the concentration range 0.1–0.4 g/dl, at $T = 25 \pm 0.05$°C.

RAMAN: CEMA samples were characterized by Raman spectrometry, Using a Bruker RFS-100 spectrometer and following the band assignments given by Marsano, De Paz, Tambuscio and Bianchi (1998).

SEC: The measurements were performed on a Waters mod. 950 A-I SEC apparatus equipped with four μ-styragel columns and a refractive index detector (Bianchi et al., 1998). A calibration curve based on PMMA standards was used.

3. Results and discussion

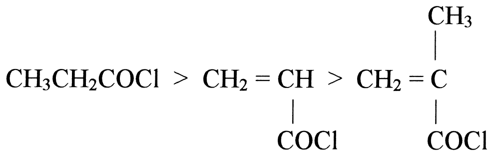
As mentioned in Section 1, the synthesis of MMA-grafted cellulose copolymers was performed following the procedure previously described for AN grafting onto cellulose samples (Bianchi et al., 1998). In general, the method is based on the preliminary reaction between CE, dissolved in DMAc containing LiCl, and an unsaturated acyl chloride (RCOCl) in order to introduce a known amount of pendant double bonds along the chain and make CE behave similar to a macromonomer. The risk of undesired CE crosslinking was avoided by adopting suitable experimental conditions (described below). Subsequently, the unsaturated monomer is added and, by the action of a suitable initiator, grafted onto the aforementioned double bonds by free radical copolymerization. In the present system, MACl was used as acyl chloride in the first step, and MMA and AIBN as monomer and initiator, respectively, in the second step.

On the basis of Eq. (1) (see Section 2), cellulose DS can vary from 0 (unsubstituted cellulose) to 3 (totally substituted sample). The most relevant parameter, which determines the actual DS values, was found to be the molar ratio of RCOCl to the number of glucosidic units, at a specific reaction time and at a fixed temperature.

Our results are given on Fig. 1, together with those previously obtained for propionyl chloride (Bianchi, Marsano, Ricco & Conio, 1997) and acryloyl chloride (Bianchi et al., 1998). The dotted line gives the maximum feasible yield, corresponding to the reaction of RCOCl with all the –OH groups of the glucosidic ring. Fig. 1 shows how the order of reactivity decreases from left to right:

Table 1
Grafting yield for the system CEMA/MMA ($T_p = 60°C$, $t_p = 6$ h; MMA/AIBN (mol/mol) = 30; MA = molar content of the methacrylate groups in the modified CE sample)

CE-g-PMMA sample code	DS	CEMA% (w/w)	MMA/–MA (mol/mol)	GP% (w/w)
1	0.94	1.10	20	603
2	0.42	0.35	16	100
3	0.29	1.10	20	282
4	0.45	0.60	16	220
5	0.36	0.60	20	222
6	0.30	0.60	20	168



$$\mathrm{CH_3CH_2COCl} > \mathrm{CH_2{=}}\underset{\mathrm{COCl}}{\mathrm{CH}} > \mathrm{CH_2{=}}\overset{\mathrm{CH_3}}{\underset{\mathrm{COCl}}{\mathrm{C}}}$$

in agreement with both the decreasing electrophylicity of the carbonyl group and the steric hindrance effect of the methyl group.

As in the case of cellulose acrylate (Bianchi et al., 1998), conditions to obtain high DS values have purposely not been explored. This was done not only to avoid a rather high grafting yield during the subsequent reaction, but also to preserve the majority of intramolecular hydrogen bonds, which ensure good rigidity and desirable properties to the cellulose main chain. Under these experimental conditions, crosslinking of CEMA, carefully investigated following methods described by Marsano et al. (1998), was completely avoided, i.e. the whole system had no insoluble fraction.

Table 1 gives the synthetic conditions and the grafting yield of six samples, prepared at 60°C (reaction time: 6 h). The range of CEMA concentrations used in our experiments was rather narrow and low (from 0.35 to 1.10%, referred to the whole reaction medium) in order to avoid any gelation, whose formation is favoured by higher CEMA concentrations. Grafting yield was expressed as grafting percentage (GP%), and defined as:

$$\mathrm{GP\%} = \frac{W_g}{W_{CE}} \times 100, \tag{2}$$

where W_g and W_{CE} are the weights of the grafted PMMA (corrected for homopolymer) and CE, respectively. Indeed, GP% should be more appropriately related to W_{CEMA}. On the contrary, the –MA pendant group represents a constitutional repeat unit (CRU) of the grafted chain and is considered in the evaluation of its average length by acid hydrolysis (see later). In contrast, W_g does not include the above CRU, in order to be appropriately compared to the weight of extracted homopolymer (W_h) in Eq. (3).

From the above data, some relevant conclusions can be drawn, in order to evaluate the specific influence of DS, CEMA concentration and MMA/–MA molar ratio, respectively, on the grafting yield at constant T_p, t_p and monomer/initiator molar ratio.

By comparing samples 1 and 3, as well as samples 5 and 6, GP% clearly increases when DS is increased. Comparison of samples 2 and 4 show an analogous increase of GP% in terms of increasing CEMA concentration. What is less clear is the effect of MMA/–MA molar ratio (in the range between 16 and 20) on GP%. Comparison of samples 4 and 5 suggests a positive effect of higher values of the above ratio, which allows the GP% to remain almost constant despite the lowering of DS values. Obviously, as it appears by comparing samples 4 and 6, a further decrease in DS cannot be counterbalanced by the higher MMA/–MA ratio and leads to the lowering of GP%. The above conclusions also remain valid in terms of the accuracy and reproducibility of results.

A second series of experiment was performed in order to evaluate the effect of reaction temperature on the preliminary set of runs (Table 2). DS was kept almost constant to 0.37 ± 0.02, CEMA concentration to 0.6% (w/w), the molar ratio MMA/AIBN to 30, the molar ratio MMA/–MA to 20 and t_p time to 6 h. These experimental conditions were chosen, so that they may be compared with the literature data (Nishioka & Kosai, 1981).

From the weights of CE used and those obtained for

Table 2
Temperature effect on grafting yield and efficiency for the system CEMA/MMA (CEMA (w/w) = 0.6%; MMA/AIBN (mol/mol) = 30; MMA/–MA (mol/mol) = 20; $t_p = 6$ h)

CE-g-PMMA sample code	DS	T_p (°C)	GP% (w/w)	GE% (w/w)	W_g/W_h
7	0.39	40	103	92	11.50
8	0.38	50	151	82	4.56
5	0.36	60	222	73	2.70
9	0.35	70	177	52	1.08

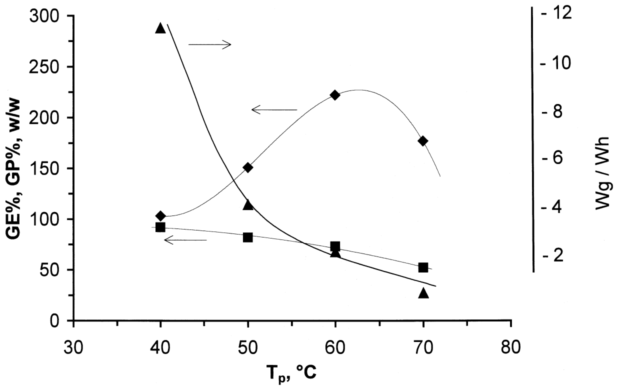


Fig. 2. GE%, GP%, W_g/W_h vs. grafting temperature T_p.

CEMA, CE-g-PMMA and PMMA homopolymer, it is possible to calculate, besides GP%, the grafting efficiency GE%, defined as:

$$\mathrm{GE}(\%) = \frac{W_g}{W_g + W_h} \times 100 \qquad (3)$$

Table 2 collects all the relevant data, including the ratio W_g/W_h, a measure of preferential occurrence of the grafting reaction, as compared to homopolymerization.

The whole set of our results is represented in Fig. 2.

As can be seen, GP% vs. T_p shows a maximum at ca. 60°C. A similar trend was observed by Nishioka and Kosai (1981) for three systems: CE–AN–ammonium persulfate in dimethylsulfoxide containing paraformaldehyde (with a maximum at 40°C); CE–MMA–ammonium persulfate in the same solvent (again a maximum at 40°C); and CE–MMA–AIBN (maximum at 60°C). However, their GP values never exceeded 100%, whilst the grafting yield is almost always much higher for the present system.

A few considerations about GE% and W_g/W_h ratio can be drawn: the smooth and regular decrease of the grafting efficiency with T_p for our system does not support the dramatic behaviour claimed in literature (Nishioka & Kosai, 1981) for the same monomer-initiator pair. Moreover, only at the highest T_p value (70°C) is the extent of the grafting reaction almost equivalent to the amount of MMA homopolymer. At lower T_p the former always strongly prevails over the latter.

Indeed, the crude comparison of data, given in Table 2 and Fig. 2, are related to the same reaction time (6 h) at different temperatures, and can be totally misleading, at least for GP%. The relevant differences in the rate of primary radical formation from AIBN dissociation, which controls the whole grafting process, have to be taken into account, as was not done for instance by Nishioka and Kosai (1981).

Table 3
Temperature effect on grafting yield for the system CEMA/MMA on the basis of equivalent reaction times ($k_d t$ = constant; CEMA (w/w) = 0.5%; DS = 0.10; MMA/AIBN = 30; MMA/–MA = 20)

Temperature (°C)	40	50	60
Reaction time	25 h, 56′	4 h, 50′	1 h
CE-g-PMMA sample code	13	14	15
GP%	11	6	0.5

In order to pay more attention on the above point, the values of the unimolecular dissociation constant, k_d, of AIBN in DMAc/5% LiCl as a function of temperature should be known. Unfortunately, k_d in this solvent mixture, as well as in neat DMAc, is unknown at any temperature. However, some data on other solvents is available in literature and allows a tentative comparison with our system: k_d in the mixture water/dioxane (20:80 v/v, pH 7) was determined at 65.3, 70, 75 and 80°C, and the activation energy E_a for the dissociation reaction derived (Masson, 1989) ($E_a = 141$ kJ/mol). Moreover, k_d in dimethylformamide, which could be considered as a solvent similar to the one used by us, at $T = 71.2$°C (Masson, 1989), and its value differs only less than 20% from that in water/dioxane at the same temperature. It is, therefore, reasonable to adopt, as a first approximation, the above values of k_d and E_a for our solvent system too.

On these grounds, a second set of experiments was performed (Table 3). DS of CEMA samples was taken as rather low (DS = 0.10) in order to reduce the MMA grafting. Moreover, the equivalent reaction time (see Table 3) was also kept low (1 h at 60°C). For the above conditions, a regular decrease in GP% is observed. We may, therefore, conclude that grafting yields showing maxima as functions of T_p are only artifacts, due to erroneous experimental setups.

Data at constant T_p, can still be safely used to calculate the average length of grafted chains. In fact, the same amount of grafted polymer with respect to CE weight, may be due to either many short or few long branches. As the physical properties of the two kinds of copolymer are quite different, it is important to know the number (n_g) and the molecular weight ($M_{n,g}$) of grafts per CE chain.

In the case of heterogeneous grafting, it was shown that M_w of grafted chains may either be much higher or of the same order or much lower than M_w of homopolymer, depending on the specific system. Numerous examples were collected by Hebeish and Gutrie (1981).

Three samples of PMMA homopolymer were synthesized in neat conditions, i.e. in the absence of CEMA, at 50, 60 and 70°C in the same conditions as those reported in Tables 1 and 2 for the copolymer synthesis. Their molecular weights were determined, both by viscometry in benzene at 25°C using the relationship $[\eta] = 5.5 \times 10^{-3} M_v^{0.76}$ (Wunderlich, 1989), and by SEC in DMF (see Table 4). The values obtained by the two methods are in good agreement and, as expected, show a decrease in molecular weight as T_p increases. If these values are now compared to those of the homopolymers formed during copolymer synthesis (i.e. the molecular weights of PMMA samples extracted from the reaction products in the second reaction step), we find from

Table 4
Molecular weights of PMMA homopolymer, synthesized at different T_p

Sample code	T_p, °C	[η] dl/g	M_v	M_{peak} SEC
PMM 1	50	0.145	31.800	32.800
PMM 2	60	0.067	11.500	12.200
PMM 3	70	0.039	5.600	6.700

the data given in Fig. 3 that the latter is always a little lower than the former. Indeed, it is reasonable to find that the presence of CEMA, even in the diluted conditions used in our experiments, affects the medium viscosity and polarity and alters the reaction parameters that control the PMMA chain length. The above variation of PMMA molecular weights, as functions of the experimental conditions, confirms the risk of extrapolation or of any arbitrary assumption on the chain length of grafts, based on homopolymer data (either in neat conditions or in the presence of cellulose).

Only a direct measurement of the grafted PMMA molecular weights can provide a quantitative evaluation of the average number of grafts per CE molecule. The adopted procedure is based on the hydrolysis of CE-g-PMMA samples by using 72% H_2SO_4 at low T (Ide, 1961). A preliminary test on PMMA alone shows that no hydrolysis is present under the same conditions. After treating the graft copolymer with H_2SO_4 for about 6 h, the cellulosic chains are expected to be completely degraded and PMMA may be recovered by water precipitation. After washing and drying, the precipitate is dissolved in benzene and its intrinsic viscosity measured. The molecular weight values for samples synthesized at 50 (sample 8), 60 (sample 6) and 70°C (sample 9), respectively, are also given in Fig. 3. The results are quite interesting because they show that, for our system, only at low T_p the molecular weight of the grafted PMMA is effectively the same as that of the PMMA homopolymer produced during synthesis. At higher T_p, however, the grafts tend to be significantly longer than the homopolymer chains. The above differences are not easily explicable.

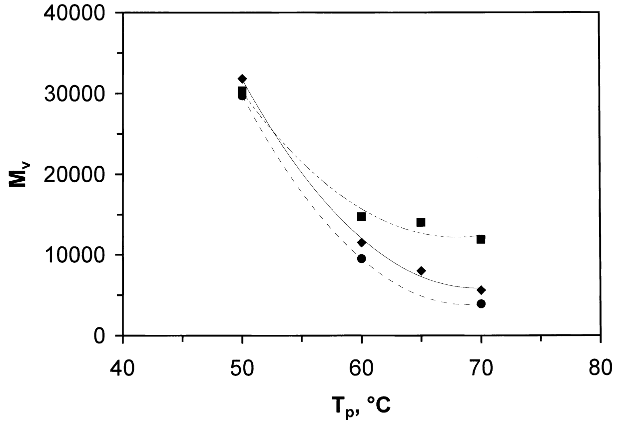


Fig. 3. Viscometric molecular weight (M_v) as a function of T_p for homopolymerized PMMA (◆), extracted PMMA (●) and PMMA grafted chains (■).

The evalutation of the average number of grafts per cellulose molecules, n_g, is based on the following equation:

$$n_g = \frac{W_g M_{n,CE}}{M_{n,g} W_{CE}} \tag{4}$$

where $M_{n,CE}$ and $M_{n,g}$ are the number average molecular weight of CE and g-PMMA, respectively.

It may be relevant to observe that Eq. (4) is often applied without mentioning the kind of average used to calculate the molecular weight. In some cases, M_w (obtained from light scattering) or M_{sd} (obtained from sedimentation and diffusion experiments) are used instead of M_n. Obviously, this procedure may lead to appreciable miscalculations, when the cellulose sample and the grafted polymer have quite different molecular weight distribution (MWD).

As a consequence, we need to know the MWD of our underivatized CE and of the grafted PMMA. MWD of CE was recently determined by M. Terbojevich et al. (in press), who performed the SEC experiments of tricarbanylate CE derivative, synthesized on purpose. The result of the size exclusion chromatography was MWD = 2.4. This value was assumed to be valid for our sample also, which belongs to the same stock. MWD of grafted and homopolymerized PMMA (sample 9, T_p = 70°C) was determined by SEC analyses in dimethylformamide which gave the values of 2.30 and 2.36, respectively. This result suggests that the MWD of grafted and homopolymerized PMMA is about the same. By introducing the values 2.40 and 2.36 for CE and g-PMMA, respectively, in Eq. (4), n_g was found to be ~6. No data was available at the moment for different values of T_p. Nevertheless, considering the fact that the MWD is almost a constant in all cases, the use of M_w instead of M_n would lead to the same results. Consequently, n_g may also be calculated at temperatures lower than 70°C, resulting in values 2.0 (at 50°C) and 6.0 (at 60°C). This specific point obviously needs further investigation.

As a final observation, it may be useful to remember that, in heterogeneous systems, grafting occurs only in amorphous regions, causing the number of grafts per cellulose chain to seldom exceed unity (Ogiwara & Kubota, 1968). In a homogeneous system, when the solvent is dimethylsulfoxide + paraformaldehyde, the maximum n_g obtained with AIBN as initiator was found to be 1.3 (Nishioka & Kosai, 1981). The values obtained for our system are much higher, and emphasises both the relevance and the potential of our homogeneous grafting method.

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