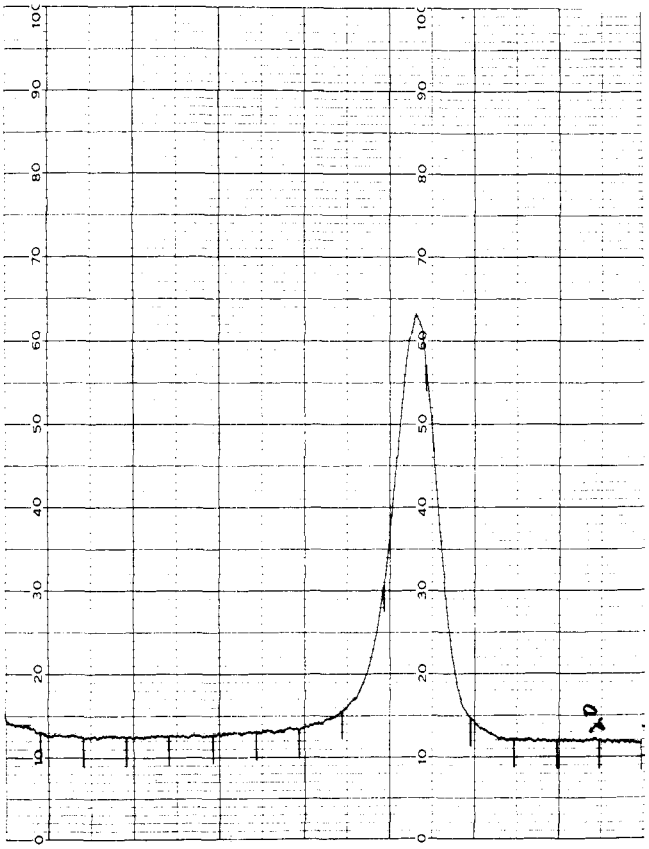

Figure 1. GPC chromatogram of poly(styrene–butadiene–styrene).

diene block was polymerized in the same manner as that described in the gelation test. In one run the presolubilization of the initiator dispersion was used as described. In a second run the presolubilization step was omitted and the entire amount of butadiene monomer was introduced prior to the addition of the initiator dispersion. After the completion of butadiene polymerization the reaction mixture was cooled to approximately 35 °C. Purified styrene monomers of approximately one-third of the weight of the butadiene used and 2 mL of freshly distilled tetrahydrofuran were added. Polymerization of styrene took another hour. After glacial acetic acid was used to terminate the anions, the copolymer was recovered by precipitation with methanol and drying under vacuum. The GPC chromatograms of both runs were nearly alike. Figure 1 shows the chromatogram for the second run in which the initiator dispersion was used directly. The calculated M_w/M_n ratio for this run was 1.4, broader than the M_w/M_n ratio of 1.2 for the first run in which the initiator dispersion was solubilized before use. The compression molded specimens of both samples gave nearly alike tensile properties: tensile rupture strength of over 3200 psi and total elongation of over 950%. These properties are comparable to those reported elsewhere[13,14] for poly(styrene–butadiene–styrene).

The above results convinced us that the addition products of *sec*-butyllithium and double 1,1-DPE compounds are useful dilithium initiators.

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Radiation Degradation of Poly(methacrylates)

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Received December 13, 1977

Methacrylate polymers have been the subject of many investigations concerning polymer radiation degradation induced by exposure to ionizing radiation.[2a] Poly(methyl methacrylate), PMMA, has been the most extensively studied and is found to predominately degrade with essentially no concurrent cross-linking.[2b,3] Graham has looked at the radiation behavior of several other poly(alkyl methacrylates) and reported that significant yields of concurrent cross-linking occur when the alkyl group is long and not branched.[4] Kircher et al.[5] find that the four isomeric butyl methacrylate polymers also predominately degrade; ester group loss and chain scission processes, however, were determined to be dependent upon ester group structure.

PMMA is an important polymer to the electronics industry because it functions as a high-resolution e beam[6] or x-ray[7] resist and is capable of integrated circuit element pattern delineation production processing. Since it has been shown that radiation G values correlate with e-beam sensitivity,[8] we report the radiation G values for several other methacrylate polymers of interest on the basis of their chemical structures.

Poly(*tert*-butyl methacrylate), PTBMA, and poly(isobutyl methacrylate), PIBMA, isomeric methacrylate polymers, are reinvestigated because they were previously reported to be more sensitive toward radiation degradation than PMMA[5] on the basis of chemical analysis and molecular weight determinations. Unfortunately, only one absorbed dose, namely 30 Mrad, was employed for these determinations and the polymers had fairly low unirradiated molecular weights; for this reason, no radiation G values were reported from the molecular weight data. We have irradiated PTBMA and PIBMA to a series of lower doses, where the determined $\overline{M}_n^{-1}$ values are linear with dose, to obtain quantitative G values for comparison to the G value of PMMA. In addition, we report results for poly(benzyl methacrylate), PBZMA, poly(cyclohexyl methacrylate), PCHMA, and copolymers of *n*-hexyl methacrylate (NHMA) and methyl methacrylate. The latter systems were chosen over PNHMA to insure that all test polymers had glass transition temperatures above room temperature.

Poly(*tert*-butyl methacrylate) (PTBMA) and poly(benzyl methacrylate) (PBZMA) were obtained from Aldrich Chemical Co., and Polysciences, Inc., respectively. The polymers were purified by twice precipitating them from solvents. Both the homopolymer poly(cyclohexyl methacrylate) (PCHMA) and the copolymers of *n*-hexyl methacrylate and methyl

0024-9297/78/2211-0617$01.00/0

Table I
G_s or $G_s - G_x$ Results for Irradiated Methacrylate Polymers

Polymer	Composition	Unirradiated $\overline{M}_n$	Unirradiated $\overline{M}_w/\overline{M}_n$[a]	T_g, °C	$G_s - G_x$
Poly(MMA-*co*-HMA)-A	80% MMA, 20% HMA	87 000	2.1	67	0.87
Poly(MMA-*co*-HMA)-B	41% MMA, 59% HMA	141 000	1.9	47	0.62
Poly(MMA-*co*-HMA)-C	28% MMA, 72% HMA	168 000	2.5	30	0.53
Poly(HMA)	100% HMA			−5	0.38[b]
Poly(cyclohexyl methacrylate)	100%	173 000	2.4	90	0.44
Poly(benzyl methacrylate)	100%	409 000	2.8	54	0.29
Poly(isobutyl methacrylate)	100%	120 000	1.7	53	1.1, 0.74[a]
Poly(*tert*-butyl methacrylate)	100%	65 000		118	1.28
Poly(methyl methacrylate)	100%	159 000	2.5	105	1.3,[c] 1.26

[a] GPC data. [b] Extrapolated value and not experimentally determined. [c] MOSM data obtained using Mechrolab osmometer 501 and THF for solvent. All other $G_s - G_x$ values obtained from MOSM data obtained by Wescan Model 230 osmometers in MEK.

methacrylate, poly(HMA-*co*-MMA), were polymerized in a chlorobenzene solution using AIBN (2,2′-azobis(isobutyronitrile)) as a free-radical initiator.

The chemical composition of each copolymer was determined by elemental analysis. The carbon, oxygen, and hydrogen content of each polymer was determined by Galbraith Laboratories, Inc. Polymer samples were sealed at $P < 10^{-4}$ mmHg into Pyrex tubes for γ irradiation at 25 °C in a Co^{60} vault at dose rates from 0.01 to 0.3 Mrad/h. Membrane osmometry, MOSM, measurements were made at either 25 or 28 °C in MEK using either a Wescan Model 231 or Model 230 recording osmometer.

Radiation $G_s - G_x$ values are obtained as described previously,[9,10] where G_s is the number of bond scissions and G_x the number of intermolecular cross-links formed per unit absorbed dose. This analysis allows comparison of different polymers under equivalent conditions for the assessment as to which is most susceptible to net radiation degradation on the basis of radiation-induced number-averaged molecular weight, $\overline{M}_n$, changes. $G_s - G_x$ values calculated from $\overline{M}_n^{-1}$ vs. dose slopes for the polymers of this work are listed in Table I.

As expected, the highest $G_s - G_x$ values were determined for PTBMA, PIBMA, and PMMA, while much lower values occurred for the other methacrylate polymers. These results clearly indicate that the smaller or shorter the ester alkyl group, the greater is the predominance of scission. The effect of increasing the *n*-hexyl methacrylate copolymer composition is to reduce $G_s - G_x$. Since the polymers studied only differ in the ester alkyl group, this reduction probably reflects an increase in G_x only; G_x may be approximated from $G_x = 1.3 - (G_s - G_x)$ (from experimental data). $G_s - G_x$ values are governed by the percent *n*-hexyl methacrylate or more generally by the polymer ester R group.

Turning now to the results for the isomeric butyl methacrylate polymers, it appears that the $G_s - G_x$ values from Table I differ from those calculated from the results of Unger et al.[11] If it is assumed that $\overline{M}_n^{-1}$ vs. dose is linear to 30 Mrad for their data, $G_s - G_x$ values of 2.5 and 2.9 are calculated for PIBMA and PTBMA, respectively. Although quantitatively these results disagree with those of Table I, they have the same relative order and equivalent PIBMA/PTBMA ratios. The ratio for the results of Unger et al.[11] is 0.86 while the ratio for values from Table I is 0.84. Therefore, the relative results are qualitatively consistent and in agreement.

Irradiated PIBMA samples were also analyzed by the GPC technique employing THF as solvent phase. Due to the lack of Mark–Houwink constants for PIBMA in THF the constants for PMMA were used to determine a universal calibration curve for PMMA for molecular weight analysis; secondary PMMA standards analyzed using this curve gave $\overline{M}_n$ values within 6%. Although accurate $\overline{M}_n$ results cannot be obtained for PIBMA samples using a PMMA calibration curve, relative changes in $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ can be monitored; GPC $\overline{M}_n$ values for PIBMA samples were systematically 40% too high vs. the $\overline{M}_n$ values obtained by MOSM. $G_s - G_x$ calculated from the GPC $\overline{M}_n$ values was 32% lower than the values obtained from MOSM data (see Table I). Interestingly, the GPC $\overline{M}_w/\overline{M}_n$ values remained constant at 1.7 (2.3 if $\overline{M}_w$(GPC)/$\overline{M}_n$(MOSM) is used) with increasing dose, thus qualitatively indicating that the molecular weight distribution is not changing and that G_x is close to zero. Further evidence for small PIBMA G_x comes from the GPC analysis $\overline{M}_w^{-1}$ vs. dose and $\overline{M}_n^{-1}$ vs. dose results; from that data for PIBMA, G_x is approximated to be −0.02 or 0 using the equation developed by Kilb[10] and the standard $G_s - G_x$ equation.

G_s values ranging from 1.1[12] to 1.9[13] have appeared in the literature for PMMA. More recently, however, Gipstein et al.[14] have reported $G_s = 1.3 \pm 0.1$ for PMMA, obtained for a carefully selected series of samples. This latter value is in excellent agreement with the values of 1.3 and 1.26 of Table I. It appears then that 1.3 ± 0.1 is the most probable experimental value for G_s in PMMA. The higher values appearing in older literature may be attributed most likely to dose calibration errors. We have observed that systematic errors of 17% in $\overline{M}_n$ can lead to errors of 28–31% in the determination of G_s or $G_s - G_x$.

The earlier interpretation of $G_s - G_x$ changes does not apply to results for poly(benzyl methacrylate) because energy absorption in this polymer system is much different than for the aliphatic systems. The conjugated ester R group has the ability to protect the polymer against main-chain scission by converting part of the absorbed ionizing radiation energy into electronic emission. This is the well-known "sponge effect"[15] and accounts for the lower observed $G_s - G_x$ value for PBZMA.

The small $G_s - G_x$ value of PCHMA is somewhat surprising. It was thought that the steric effect induced by the presence of a bulky cyclohexyl group in the side chain could possibly enhance the radiation degradation of the polymer. However, our GPC studies indicate that molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of irradiated PCHMA increases steadily with an increase in radiation dose and at a dose of 38 Mrad, the $\overline{M}_w/\overline{M}_n$ value is increased from 2.4 for the unirradiated polymer to 6.1 for the irradiated polymer. Similarly an increase in $\overline{M}_w/\overline{M}_n$ value with an increase in radiation dose was also observed for PBZMA. For PBZMA, the $\overline{M}_w/\overline{M}_n$ value is increased from 2.8 for the unirradiated polymer to 3.6 for the irradiated polymer at 5.1 Mrad. The broadening of molecular weight distribution clearly suggests that upon irradiation both polymers, PCHMA and PBZMA, undergo significant concurrent cross-linking in addition to main-chain scission.

To summarize, predominant radiation degradation is observed for the systems studied; lower or equivalent degrees of degradation susceptability are, however, observed for all

systems. G_x cannot be zero for the *n*-hexyl copolymers and homopolymers PNHMA, PCHMA, and PBZMA but G_x is probably very small if not zero for the branched butyl methacrylate polymers. This is probably why the *G* values reported for PIBMA and PTBMA are so close to that of PMMA (i.e., $G_x \simeq 0$ and G_s is primarily determined by the methacrylate structure). There is no apparent effect of a large steric group at the ester R group position and G_x remains small until the alkyl group is greater than C_4. The *G* values obtained form the basis for the concluding prediction that the polymers of this study will be equivalent or less sensitive positive e-beam resists than PMMA.

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Active Esters in the Synthesis of Sequential Polypeptide Models of Collagen. An Improved Synthesis of (Pro-Pro-β-Ala)$_n$

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Received September 20, 1977

The synthesis of (Pro-Pro-β-Ala)$_n$ is of special interest as this polymer has similar ORD and CD spectra to (Pro-Pro-Gly)$_n$ suggesting a structural resemblance to collagen.[2a] In the earlier synthesis of the (Pro-Pro-β-Ala)$_n$ via the pentachlorophenyl active ester procedure,[2b] the polymer was obtained in no more than 30% yield and the weight average molecular weight was 6500 ($n \simeq 24$ to 25) or less. Subsequent attempts to synthesize the polymer resulted in variable results, and in some attempts the polymer obtained was of low molecular weight and was completely dialyzed out of the dialysis bag. Similar difficulties were experienced by Urry and Ohnishi[3] and by Bell et al.[4] in the synthesis of H-(Val-Pro-Gly-Gly)$_n$-Val-OMe via the pentachlorophenyl ester procedure. Recently, we reported the synthesis of the above polytetrapeptide in excellent yields (~90%), with $n > 40$ via the *p*-nitrophenyl active ester procedure.[5] As the *p*-nitrophenyl ester procedure proved to be superior in the synthesis of the above polytetrapeptide, the synthesis of (Pro-Pro-β-Ala)$_n$ by this active ester procedure was undertaken.

Experimental Section

(Pro-Pro-Gly)$_n$ was purchased from Miles-Yeda Co. and was purified on a polyacrylamide gel column. Thin layer chromatography was performed on silica gel G plates (Quantum Industries) with the following solvent systems: R_f^1, chloroform/methanol (1:1, v/v); R_f^2, chloroform/methanol (10:1 v/v); R_f^3, chloroform/methanol/acetic acid (95:5:3, v/v); R_f^4, *n*-butyl alcohol acetic acid/water (4:1:1, v/v); R_f^5, *n*-butyl alcohol/pyridine/water (7:3:1, v/v); R_f^6, *n*-butyl alcohol/acetic acid/water/pyridine (30:6:20:24, v/v). The carbon-13 magnetic resonance spectra were obtained on a JEOL PFT-100 pulse spectrometer operating at 25.15 MHz with proton noise spin decoupling and an internal deuterium lock.

The synthetic scheme of the polymer is given below:

Boc-Pro-Pro-β-Ala-OH

$$\xrightarrow{CF_3COOC_6H_4NO_2} \text{Boc-Pro-Pro-β-Ala-ONp} \quad \text{(I)}$$

$$\text{I} + CF_3COOH/CH_2Cl_2 \longrightarrow F_3AcOH\cdot\text{H-Pro-Pro-β-Ala-ONp} \quad \text{(II)}$$

$$\text{II} + NEt_3 \longrightarrow \text{(Pro-Pro-β-Ala)}_n \quad \text{(III)}$$

$$\text{III} + HCOOH/(CH_3CO)_2O \longrightarrow HC(\text{Pro-Pro-β-Ala})_n \quad \text{(IV)}$$

Boc-Pro-Pro-β-Ala-ONp (I). This compound was synthesized from Boc-Pro-Pro-β-Ala-OH (2.3 g, 6 mmol) and *p*-nitrophenyl trifluoroacetate (3.95 g, 16.8 mmol)[6] in pyridine following the procedures described earlier[5] to obtain 2.0 g (66%) of an extremely hygroscopic product: R_f^1, 0.86; R_f^2, 0.89; R_f^3, 0.66. Anal. Calcd for $C_{24}H_{32}N_4O_8\cdot\frac{1}{2}H_2O$: C, 56.13; H, 6.47; N, 10.90. Found: C, 56.12; H, 5.92; N, 10.42.

F_3AcOH·H-Pro-Pro-β-Ala-ONp (II). Compound I (1.8 g, 3.5 mmol) was dissolved in 50% trifluoroacetic acid in dichloromethane (15 mL) and processed as described earlier[5] to obtain an extremely hygroscopic amorphous powder: 1.72 g (95%); R_f^4, 0.25; R_f^5, 0.54; R_f^6, 0.38. The product was used as such in further synthesis.

(Pro-Pro-β-Ala)$_n$ (III). Compound II (403 mg, 0.8 mmol) was dissolved in dimethyl sulfoxide (1.2 mL). Triethylamine (0.22 mL, 0.16 mmol) was added dropwise to the vigorously stirring solution. After 14 days of polymerization, the reaction mixture was diluted with 3 mL of dimethyl sulfoxide and the reaction mixture was dialyzed for 7 days against several changes (14 × 2000) of distilled water and lyophilized to yield 159 mg (75%) of polymer; mp, the compound showed a color change at 75 °C and decomposition at 260 °C; R_f^4, 0.1; R_f^5, 0.88; R_f^6 0.16. Anal. Calcd for $C_{13}H_{19}N_3O_3\cdot\frac{2}{3}H_2O$: C, 56.00; H, 7.41; N, 15.12. Found: C, 55.59; H, 7.02; N, 15.12. Amino acid analysis: Pro, 2.00; β-Ala, 0.96.

Formyl-(Pro-Pro-β-Ala)$_n$ (IV). Compound III (45 mg) was formylated as described earlier[5] to obtain 31 mg of formylated product: R_f^4, 0.16; R_f^6, 0.26. Amino acid analysis: Pro, 2.00; β-Ala, 0.98. The compound was shown to have an average $n > 40$ by NMR analysis of end groups.[3,7,8]

Results and Discussion

The ^{13}C NMR of I is presented in Figure 1A, and it was shown to be of sufficient purity for polymerization, as utilization of pure intermediates is of critical importance to obtain good yields of large molecular weight polymers.[9] The ^{13}C NMR of the polymer, III, is presented in Figure 1B. Utilization of the *p*-nitrophenyl ester procedure in the synthesis of the polymer resulted in good yields (an average yield of 71%) and the polymers were shown to be of large molecular weight ($n > 40$). The *p*-nitrophenyl ester method produced not only good yields of higher molecular weight polymers but was also shown to yield reproducible results in three separate attempts (see Table I).

It is reasonable to consider[5] that the superiority of *p*-nitrophenyl ester to pentachlorophenyl ester be due to the fact that the pentachlorophenyl esters are comparatively more activated, hence more likely to be decomposed by higher concentrations of base, thereby terminating the polymerizing species prematurely. Another reason might be that H-Pro-Pro-β-Ala-OPcp is a more active ester than the corresponding *p*-nitrophenyl ester and that in the former the tendency to form prolylprolyl diketopiperazine with simultaneous

0024-9297/78/2211-0619$01.00/0