H. R. Anderson, Jr.
E. A. Bartkus
J. A. Reynolds

Molecular Engineering in the Development of Materials for Thermoplastic Recording

Abstract: A number of internally plasticized copolymers and terpolymers have been prepared which are shown to be suitable for thermoplastic recording. These materials were responsive to both in-air and in-vacuum recording techniques, where the electrostatic charge is applied by corona charging or electron beams, respectively. Several of these materials were tailored for Schlieren optical readout while others possessed properties suggesting their use in recording systems requiring electron beam readout.

Introduction

Several years ago, W. E. Glenn of the General Electric Company described an imaging technique which he called thermoplastic recording [1]. Briefly, an electrostatic charge on the surface of a thermoplastic polymer film creates an attractive force with an internal image charge. Heating the polymer causes material to flow under the influence of this attractive force; as a result, a depression forms in the area of the original charge, and displaced material is forced to the edges of the depression. Rapid cooling of the film prevents further flow and yields a stable pattern of deformations that reproduces the original pattern of electrostatic charges. In a second heating step, usually at a higher temperature than the first, there is a reverse flow of material, mostly due to surface tension. The surface of the polymer film becomes smooth again, and the recorded pattern is erased. This recorded information is read out by using Schlieren optics or an electron beam.

This technique for recording information places a number of requirements on the thermoplastic polymer film used as the medium, if it is to respond reproducibly over a large number of record/erase cycles. First, it must be resistant to thermal degradation. Second, its electrical properties should be resistive enough to prevent dissipation of the electrostatic charges before deformations can occur. Since the pattern of electrostatic charges can be generated subtractively (e.g., by selective photoconductive destruction of a uniform surface charge) or additively (e.g., by an electron beam), it follows that the method of charge application and readout may require that the polymer be photoconductive as well as resistant to radiation damage. Further, the polymer film must be free of low-molecular-weight species that would migrate in the vacuum environment to cause changes in polymer properties and contamination of the electron gun. Finally, the glass transition temperature T_g of the polymer must be high enough to prevent loss of deformations during storage.

This paper describes the results of a series of experiments conducted to develop materials for thermoplastic recording. The experiments were concerned chiefly with two properties of materials: their molecular structure as it affects the desired response, and their resistance to degradation caused by the combined effects of radiation and thermal degradation.

Experiment

- *Synthesis of thermoplastic recording materials*

The polymer samples used in this program were synthesized in toluene solution by using AIBN [2, 2^1-azobis (2-methylpropionitrile)] as a free radical initiator. This polymerization scheme was chosen to ensure the random structure that generally permits the production of optically clear material. Polymerization was carried out at 67°C for forty-eight hours. Solid t-butyl catechol was added to quench the reaction and serve as an antioxidant. The reaction mixture was diluted with an equal volume of toluene. To precipitate the polymer, the mixture was then added drop by drop to cold methanol (−78°C) with constant stirring. Solid polymer was recovered either by filtration or by allowing the polymer slurry to agglomerate as it warmed to room temperature. The material was dried in vacuo and used without further purification. Throughout this report, compositions of polymers referred to are actually monomer ratios in mole percentages. Pyrolytic gas chromatographic analyses of the polymers showed that these composition identifications were satisfactory.

- *Characterization of polymers*

Molecular weight

Polymer samples were characterized by their number average molecular weight $\bar{M}_n$ by means of a vapor pressure osmometer (VPO) calibrated with biphenyl. The molecular weight was determined by using three to five different concentrations of the polymer in toluene solution and graphically extrapolating these data to zero concentration.

Gel permeation chromatography

The number average size $\bar{A}_n$, weight average size $\bar{A}_w$, and molecular weight distribution were determined by using a gel permeation chromatograph (GPC). This instrument was equipped with four columns in series having average packing pore sizes of 10^6, 10^4, 10^3 and 400 Å. Tetrahydrofuran was used as a carrier solvent. The instrument was calibrated with standard polystyrene and polypropylene glycol samples.

Viscosity

The melt viscosity of the polymer samples was measured by using a plate-cone viscometer. A two-piece copper block surrounding the heating jacket, plate and rotor cone gave uniform temperature control. The copper block was equipped to maintain an atmosphere of inert gas (nitrogen) during the measurements. Temperature was measured by an iron-constantan thermocouple in the plate assembly immediately below the polymer melt.

- *In-air recording equipment*

Equipment was constructed to determine the response characteristics of thermoplastics in air. This equipment consisted of a corona discharge unit, a ground plane in the shape of a grid, a hot-air development unit, and a Schlieren optical system. The method for determining response characteristics of thermoplastics was the following. The thermoplastic material was coated from toluene solution onto a transparent flexible film substrate by means of a technique similar to doctor blading. Rods wrapped with wire of various gauges were used to control the thickness of the coating. After the solvent was completely removed, the film was placed in a special holder in the Schlieren optical system. The charge pattern applied to the film by the corona discharge system was controlled by the spacing in the ground-plane grid. The in-air response data reported here were obtained for a spacing of 100 lines/in. During development of the pattern by a hot air pulse, the intensity of the light produced by surface ripples was measured electronically; the temperature attained at the film surface was measured with a thermocouple. These measurements yielded a rate of response value (mV of light output per msec) as well as the temperature of deformation T_d, and the temperature of erasure T_e.

- *In-vacuum write-develop-erase cycling techniques*

Write-develop-erase cycling tests of thermoplastic media were carried out with electron-beam recording equipment especially designed for this purpose. The polymer to be tested was coated from toluene solution onto a thin, transparent, electrically conductive tin-oxide surface supported by a quartz glass slide. The conductive coating was used as a resistive heater to develop and erase the image. By means of automatic controls, the slide was subjected to the following procedure.

First, the electron beam was swept across the polymer coating in a series of parallel lines over an area approximately one-half inch square. When a nominal one-mil-diameter beam was used, the maximum image density was about 375 lines per inch.

Next, the electron beam was blanked out and a current pulse was sent through the resistive coating to develop the image thermally. After a short delay, a longer current pulse erased the image. The temperature profiles as a function of time were measured with a high-speed recorder connected to an iron-constantan thermocouple attached to the tin oxide coating with a drop of epoxy resin. After another delay to allow the plate to cool, the cycle was repeated. The image was observed visually and recorded by means of photographs using a transmitted-light projection system. Changes in polymer response could therefore be detected and separated from any system operation changes.

Results and discussion

- *Response characteristics of selected thermoplastic systems*

Figure 1 shows that the molecular weight of a polymer has a pronounced effect on its response to electrostatic forces. It was also discovered that the plasticizer content had a pronounced effect on the response characteristics. Table 1 shows results which demonstrate that the rate of response can be enhanced, and the temperature at which deformation takes place can be lowered, by increasing plasticizer content. Table 2 shows results that confirm the a priori feeling that the response characteristics depend on the magnitude of the corona charging voltage. Note also that T_d decreases with the magnitude of the charging voltage. Finally, Fig. 2 shows the importance of the thickness of the thermoplastic coating.

Table 1 Effect of plasticizer (o-terphenyl) content on the response characteristics of polystyrene in thermoplastic recording*.

Polymer	*o-Terphenyl (phr)‡*	T_d *(°C)*	ΔT*§ (°C)*	*Rate of response (mV/msec)*	*Light output (mV)*	*Remarks*
Polystyrene†	5	175	55	0.42	83	—
Polystyrene†	10	160	60	0.64	91	—
Polystyrene†	20	115	85	0.70	98	—
Polystyrene†	40	110	70	1.30	118	—
Polystyrene†	100	room temp.	—	—	111	plasticizer crystallizes out

* Tested at a charging voltage of 1200 V.
† Dow PS-2 resin ($\overline{M}_n = 3310$)
‡ phr = parts plasticizer per hundred parts resin, by weight
§ $\Delta T = T_e - T_d$

Although the electrostatic force increases with a decrease in coating thickness, the observed response rate of the thermoplastic material does not behave accordingly. Apparently the interface between the coating and the substrate has a limiting effect, which is not well understood. A coating of about 0.6 mils must be used to avoid a sluggishness in response imposed by the proximity of the film surface to the interface. The sluggishness further manifests itself by limiting the light output, which is related to the depth of film deformation before signal saturation.

- *Styrene-methacrylate copolymers*

Internal plasticization of the polymer system is the key to long-term cycling in a high-vacuum system. Additional considerations involve the response of the internally plasticized polymers to radiation exposure. In general, polymers fall into two classes with respect to their response to radiation: those that cross-link and those that undergo scission. The cross-linking type will increase in molecular weight to cause the recording characteristics to become progressively more sluggish to the point of no response. Predominant scission will turn the polymer to "soup". Everything else being equal, the ideal thermoplastic material is one in which the cross-linking and scission effects balance one another to preserve the initial bulk viscosity properties. Another important consideration is the *G*-value, i.e., the number of chemical events occurring per 100 eV of exposure. Aromatic materials as a class are the most radiation-resistant organic compounds. In the styrene-methacrylate copolymers investigated, the styrene portion is very radiation-resistant, but as a homopolymer it cracks and crazes and will undergo progressive cross-linking when exposed to radiation. Introducing methacrylate units causes styrene to plasticize internally and lowers the glass transition temperature. In addition, certain

Figure 1 Log (rate of response) vs the reciprocal of the number average molecular weight ($\overline{M}_n$) of polystyrene plasticized with o-terphenyl (40 phr) at a charging voltage of 1200 volts.

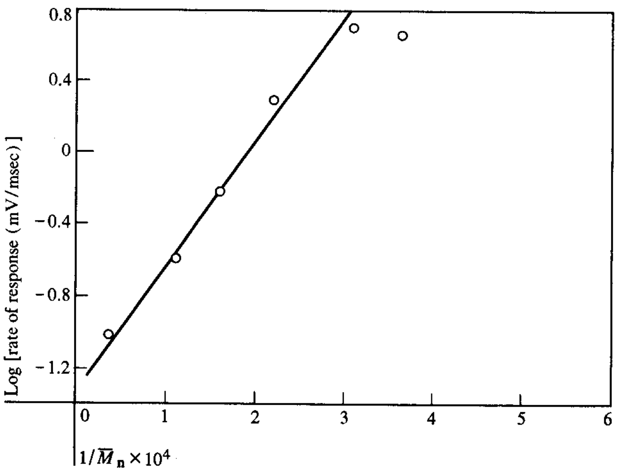


Figure 2 Effect of the coating thickness on the rate of response and the optical signal at a charging voltage of 1200 volts for polystyrene ($\overline{M}_n = 3310$) plasticized with o-terphenyl (40 phr). (* A wire-wrapped draw rod was used to control thickness. Changing wire size changes thickness.)

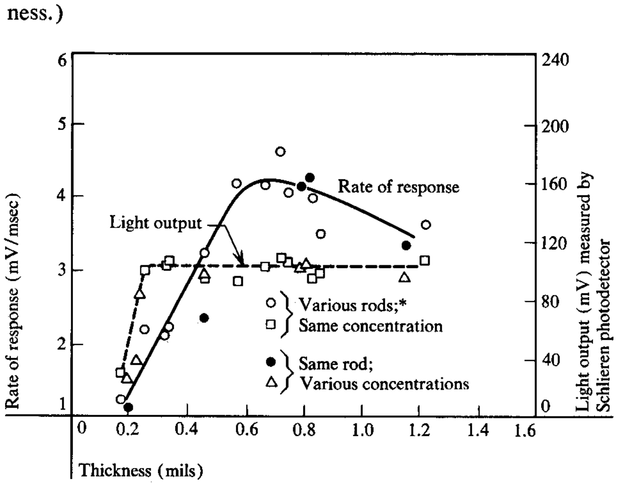


Table 2 Effect of charging voltage on the response characteristics of polystyrene* plasticized with o-terphenyl (40 phr).

Thickness (mils)	*Charging voltage (volts)*	T_d *(°C)*	ΔT *(°C)*	*Rate of response (mV/msec)*	*Light output (mV)*
0.64	1200	104	42	3.51	113
0.64	1000	104	41	3.58	113
0.62	800	116	31	4.81	113
0.62	600	120	25	3.16	110
0.63	400	128	37	2.42	114
0.64	200	141	62	1.01	106

* Dow PS-2 resin ($\overline{M}_n$ = 3310)

methacrylates will exhibit scission with varying effects when exposed to ionizing radiation. Therefore, the following studies were undertaken to determine the type and concentration of methacrylate molecules required to provide materials with a balance of suitable response, cyclability, and record permanence.

Rate of response experiments

The deformation temperature and the deformation rate were determined for a series of copolymers using the in-air recording equipment. (These data are summarized in Table 3.) The following conclusions can be drawn.

First, deformation temperature decreases with increasing charging voltage and charge density (this is consistent with the considerations that follow). The force between charges leading to deformation is initially resisted primarily by the viscoelastic forces of the medium. Although it is true that in the final stage of deformation, surface tension becomes the main force resisting the residual electrostatic surface charge, the T_d values reported here were taken in all cases at the initial stages of development. The rate of leakage of surface charge increases with temperature, but the viscosity, and hence the resistance to deformation, decreases more rapidly with increasing temperature. Therefore, a point is reached during the development step at which the residual electrostatic charge is capable of deforming the thermoplastic material. This point will occur at lower temperatures as the initial charge density is increased. Second, the data in Table 3 show that the expected rate of deformation increases with applied charging voltage.

The styrene-methacrylate copolymers shown in Table 3 were prepared with varying methacrylate hydrocarbon-tail lengths, methacrylate content, and molecular weights, in order to examine the effect of internal plasticization (variations in T_g) on the response of materials during thermoplastic recording.

If we ignore all structural considerations other than the effect of plasticization on T_d and the rate of deformation, the following results are anticipated: First, increasing the length of the hydrocarbon tail at constant molecular weight will decrease the deformation temperature and increase the rate of response. Next, increasing the methacrylate content at constant molecular weight will also decrease the deformation temperature and increase the rate of response. Finally, increasing the molecular weight of a given polymer will result in an increased deformation temperature and a decreased rate of response. The temperature of deformation is undoubtedly related to the glass transition temperature of the polymer, and the latter is influenced by these changes in degree and type of internal plasticization.

The data in Table 3 show that these predictions are not realized in all cases. For example, styrene-hexyl methacrylate compositions varying from 85-15 to 75-25 have T_d values at 600 V that increase with increasing methacrylate content. Furthermore, the rate of response for these materials decreases as the percentage of methacrylate is increased. This behavior may reflect a change in the electrical characteristics of these polymers, which leads to the conclusion that the advantage of lowered polymer viscosity obtained by an increase in internal plasticization is outweighed by an apparent increase in the electrical conductivity of the system.

On the other hand, styrene-octyl-decyl-methacrylate copolymers have the anticipated response characteristics in that the compositions of 90-10, 85-15, 80-20, 75-25, and 69-31 show a steady decrease in T_d through this series. The rate of response increases initially with methacrylate content, and then levels off as the apparent influence of electrical conductivity outweighs the lowered viscosity at a given temperature.

A comparison of T_d and rate of response values for styrene-ethyl, styrene-hexyl, styrene-octyl-decyl and styrene-stearyl-methacrylate copolymers with molecular weights of 3570, 3550, 3630 and 3880 respectively shows, as predicted, a steady increase in rate of response with increasing hydrocarbon tail length. T_d decreases for the first two members of this series, but increases slightly for the last two. The latter result may be due to the slightly larger molecular weight of the octyl-decyl and stearyl polymers.

The influence of molecular weight on the deformation characteristics of these copolymers is shown in the 65-35 styrene-octyl-decyl-methacrylate data in Table 3. T_d does not vary with molecular weight in any consistent manner. However, the rate of response increases as the molecular weight becomes greater. This result, while surprising when considered only from the standpoint of molecular weight-viscosity relationships, may be due to the ability of the higher-molecular-weight polymer to retain surface charge.

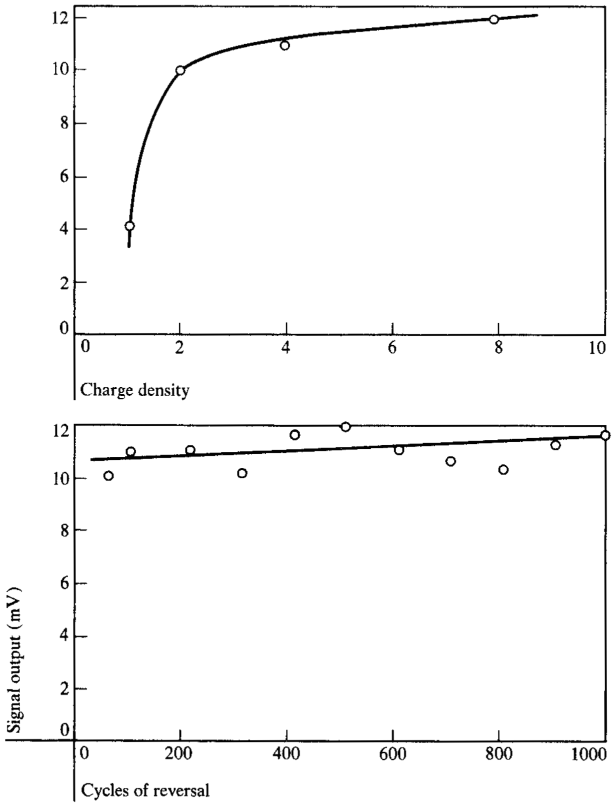
From the above discussion, it is apparent that electrical as well as rheological (flow) properties must be considered when a material is designed for thermoplastic recording.

Table 3 Response characteristics determined by in-air thermoplastic recording techniques of various styrene-methacrylate copolymer compositions.

	Composition (mole %)						*Physical properties*								
								Response characteristics							
								T_d(°C) at charging voltage of				*Deformation rate (mV/msec) at charging voltage of*			
	Styrene	*Ethyl methacrylate*	*Hexyl methacrylate*	*Octyl-decyl methacrylate*	*Stearyl methacrylate*	*2-Ethylhexyl acrylate*	$\overline{M}_n$‡	*300V*	*600V*	*900V*	*1200V*	*300V*	*600V*	*900V*	*1200V*
1	80	20					3570	148	139	142	130	0.26	0.26*	0.41	0.49*
2	85		15				2410	136	130	128	125	0.54†	0.68	0.84*	0.56
3	80		20				2610	136	130	130	123	0.87†	0.48	0.75	0.58*
4	80		20				3550	133	123	125	127	0.32	0.33*	0.33	0.35*
5	75		25				2630	147	132	135	138	0.34	0.46*	0.36*	0.53
6	95		4			1	2520	125	119	112	117	0.63	1.01	1.31	1.05
7	90			10			2530	151	154	146	147	0.18	0.39*	0.45*	0.54
8	85			15			2440	146	136	133	128	0.65*	0.70	1.12*	1.27*
9	80			20			3630	142	134	130	136*	0.35*	0.33*	0.47*	0.36
10	75			25			3280	105	95	92	97	1.13	1.55	1.75	1.51*
11	69			31			3170	83	92	75	75	1.44	0.92	1.24	1.45
12	65			35			3990	95	88	83	77	0.13	0.22	0.21	0.28
13	65			35			4930	110	116*	95	80	0.25	0.30	0.47	0.51
14	65			35			4930	87	80	80	76	1.15	1.27	1.12	0.83*
15	65			35			6510	121	83	83	83	1.05	1.23	1.20	1.20
16	65			35			—	130	128	133	126	0.55*	0.55*	0.68*	1.31†
17	60			40			3160	75	63	59	61†	0.64	0.65*	0.59*	0.86†
18	82.9				17.1		2670	112	108	110	110	1.08	1.27	1.03*	1.60
19	82.2				17.8		4025	105	110	102	110†	1.26*	0.99*	0.95	0.78†
20	81.7				18.3		2570	100	95	95	86	1.20*	2.07*	1.49	2.1 *
21	80.5				19.5		3880	145	139	145†	—	0.77	0.69*	0.75†	—
22	79				21		2710	97	87	73	73	1.17	1.17	0.84*	0.78*

* Duplicates differ by more than 20%
† One result
‡ Number average molecular weight (one point determination) by VPO technique

Figure 3 Optical output as a function of the charge density and the number of write-erase cycles with a copolymer of styrene-octyl-decyl methacrylate (80–20 mole ratio).



Cycling experiments

To establish some recording and reversal characteristics in vacuum, a number of copolymers of styrene and various methacrylates were subjected to preliminary write-develop-erase cycling tests with an electron-beam apparatus. In these tests a 15-kV electron beam was used to produce writing densities of 200 lines per inch. Figure 3 is a typical curve obtained to determine the charge density required to maximize the optical signal resulting from the deformations. Since the optical signal became saturated after a certain depth of deformation, the smallest charge density capable of producing the maximum optical signal was used. Excessive charge density serves only to expose the thermoplastic to unnecessary radiation damage and thus to limit the write-develop-erase cycling life. Figure 3 also shows the optical signal during a test of 1000 write-develop-erase cycles. Figure 4 shows the develop and erase temperatures required during the same test. These two figures show that the response characteristics were essentially unchanged during the test. Such data indicate that the material had undergone a relatively small change in its physical (viscoelastic) and electrical properties. Table 4 shows data obtained in these preliminary recording experiments with several styrene-methacrylate copolymers. All polymers survived the 1000 write-develop-erase cycles, underwent no change in response characteristics during cycling, and did not crack or craze.

The data in Table 4 show that the develop (T_d) and erase (T_e) temperatures were dependent on the amount of

Table 4 Response characteristics of several copolymers of styrene and various methacrylates during write-develop-erase cycling in a vacuum.

Type of methacrylate	*Styrene/methacrylate ratio*	$\bar{M}_n$*	T_d (°C)	T_e (°C)	ΔT (°C)
Butyl	3/2	5440	48	150	102
Hexyl	4/1	3550	48	142	94
Hexyl	3/2	3690	44	118	74
Octyl-decyl	4/1	3680	55	114	59
Octyl-decyl	3/2	3160	30	88	58

* Number average molecular weight (one point determination) by VPO technique

internal plasticization, i.e., on the amount of methacrylate and the length of its hydrocarbon chain.

It is noteworthy that the difference between develop and erase temperatures decreases with the level of internal plasticization. This feature would serve to reduce the extent of thermal degradation of the polymer's rheological properties after repeated cycling.

The conclusions drawn from the data in Tables 3 and 4 for comparable polymer systems differ in detail. It should be emphasized that the response data for the various polymers listed in Table 3 were obtained for identical charging conditions in air coupled with millisecond development times. By contrast, the response data for similar polymers listed in Table 4 were obtained in a vacuum by using various charge densities to optimize the optical signal and long (5 sec) development times. These results show that the development and erasing steps in thermoplastic recording are controlled by the time- and temperature-dependent electrical and rheological properties of the polymer.

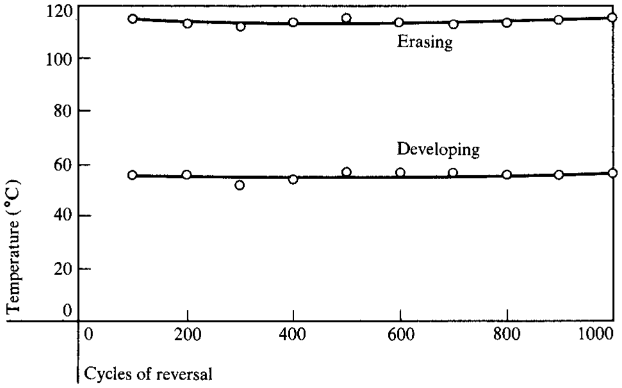
More extensive cycling was done on equipment producing higher recording density. In this case, a 10^{-8}-ampere electron beam at 5 kV was used to produce a 1-mil spot. The density of the write pattern was 375 lines/inch. A 300-msec current pulse through the conductive coating gave a peak plate temperature of 68–70°C for the develop step, and erasure was carried out by a 3-second pulse leading to a peak plate temperature of 117 to 120°C. The response and quality of lines was observed by means of a projection system which allowed the deformations to be photographed.

Styrene-butyl methacrylate (60-40), styrene-hexyl methacrylate (70-30) and styrene-octyl-decyl methacrylate (80-20) copolymers were cycled 1360, 2300 and 10,000 times, respectively, and no change in deformation characteristics was observed during the experiment. These experiments were terminated either because of time limitations or due to experimental difficulties with the apparatus, and do not represent the maximum cycling lifetimes of the polymers described. A styrene-octyl-decyl methacrylate (85-15) copolymer film was cycled 50,000 times with essentially constant operating conditions throughout the entire period. Equivalent deformations were produced at the beginning and end of the cycling period.

At the end of the cycling experiment, samples of the polymer film were obtained from the write area, which had been exposed to both the electron radiation and thermal pulsing, and from a nearby area that had received only thermal pulsing. These were analyzed by gel-permeation chromatography (GPC) and compared to the starting material. The molecular weight averages presented in Table 5 were determined from distribution curves derived from the GPC (see Figs. 5 and 6). The number average molecular weights $\bar{M}_n$, as determined by vapor pressure osmometry (VPO), are included for comparison.

The data in Table 5 show that the average molecular weight changes were small. Thermal degradation lowered the average molecular weight slightly, while combined thermal and radiation degradation caused a small rise. The changes in molecular weight distribution, as indicated by Q, the ratio of weight to number averages, show a slight spreading, mainly toward the high-molecular-weight side. This is also quite evident from the GPC distribution

Figure 4 Develop and erase temperatures as a function of the number of cycles with a copolymer of styrene-octyl-decyl methacrylate (80–20 mole ratio).



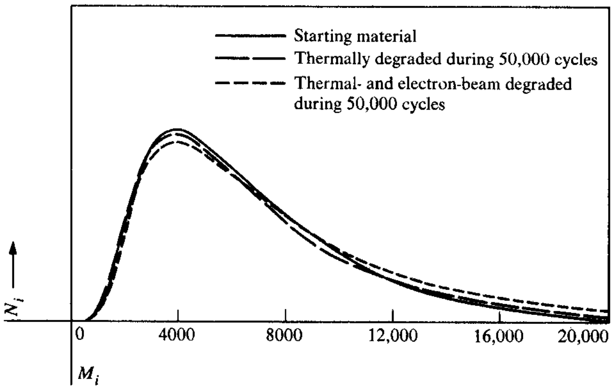


Figure 5 Molecular weight distribution curves for styrene-octyl-decyl methacrylate (85–15 mole ratio). N_i is the number of molecules of species *i*. M_i is the molecular weight of species *i*.

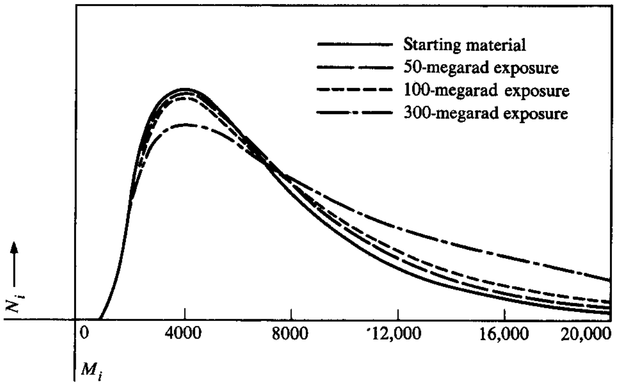


Figure 6 Molecular weight distribution curves for styrene-octyl-decyl methacrylate (85–15 mole ratio).

curves (Fig. 5). Such bulk property and cycling data indicate relatively small changes in the viscosity, and hence the responsiveness, of the recording medium.

Gamma-ray experiments

To study the effects of polymer structure on radiation resistance, we exposed five copolymers and two terpolymers of styrene, various methacrylates, and 2-ethylhexyl acrylate to 50, 100 and 300 megarads of Co-60 gamma radiation in vacuum at room temperature. Molecular size and molecular size distribution were measured by GPC for each material, and are reported in Table 6 as a function of composition and dosage. The ratio of weight to number average size, Q, was found to increase slightly for each material with increasing radiation exposure and indicates a slight broadening of the molecular size distribution. Figure 6 is a typical distribution curve for styrene-octyl-decyl methacrylate (85-15) and shows the formation of additional high-molecular-weight species when the polymer is subjected to gamma radiation. It is noteworthy that the position of the peak maximum shifts only slightly even after a dosage of 300 megarads, and the maximum Q value for this sample still represents a very sharp distribution. The terpolymers, which contain styrene, hexyl methacrylate and 2-ethylhexyl acrylate, show approximately the same increase in Q value as the present copolymers of styrene-hexyl methacrylate.

In Table 6, $\bar{A}_n$ and $\bar{A}_w$ represent the number and weight average largest dimension, and are directly related to the molecular weight. Since this relationship is different for linear from that for branched polymers, and since the originally linear macromolecules may have undergone various degrees of branching during irradiation, a direct comparison of the size parameters of the materials listed in Table 6 is not quantitatively meaningful. It is more meaningful to correlate changes in molecular size with changes in melt viscosity of irradiated materials. This is discussed in a subsequent section.

Table 5 Changes in molecular weight due to cycling and radiation degradation of styrene-octyl-decyl methacrylate (85-15) copolymer.

	$\bar{M}_n$*	$\bar{M}_n$†	$\bar{M}_w$‡	Q§
Starting material	3490	3490	4950	1.42
50K cycled-thermal degradation only	—	3390	4970	1.46
50K cycled-thermal and radiation degradation	—	3600	5400	1.50
γ-irradiated 50 megarads	3730	3620	5260	1.45
γ-irradiated 100 megarads	3680	3630	5340	1.47
γ-irradiated 300 megarads	3200	4060	5890	1.45

* Number average molecular weight (one-point determination) by VPO technique

† Number average molecular weight by GPC technique

‡ Weight average molecular weight by GPC technique

§ $Q = \bar{M}_w/\bar{M}_n$

Number average molecular weights were determined by vapor-pressure osmometry for styrene-octyl-decyl methacrylate (85-15), and are also reported in Table 6. The overall change in $\bar{M}_n$ is very small.

The authors have estimated that under the cycling conditions employed to determine the reversibility capabilities of these copolymers as films, 250,000 to 300,000 cycles are approximately equivalent to 300 megarads of gamma radiation. It can be concluded that the materials described in Table 6 can withstand at least this number of cycles without significant change in molecular size or molecular-size distribution. This assumes that the radiation effects of low-energy electrons are equivalent to those of high-energy gamma rays when compared on the basis of equal absorbed energy. It is further assumed that the

Table 6 Osmometric and gel permeation chromatographic analyses of several copolymers of styrene with various methacrylates and acrylates exposed to cobalt-60 gamma radiation.

Composition (mole %)		*1*	*2*	*3*	*4*	*5*	*6*	*7*
Styrene		85	80	75	80	80	85	80
Hexyl methacrylate		15	20	25	16	4	—	—
Octyl-decyl methacrylate		—	—	—	—	—	15	20
2-Ethylhexyl acrylate		—	—	—	4	16	—	—
Gel permeation chromatographic results								
	Dosage in megarads							
$\bar{A}_n$*	0	178	200	199	196	204	171	194
	50	203	195	189	193	195	174	196
	100	183	199	185	196	190	176	206
	300	—	209	196	187	206	190	208
$\bar{A}_w$†	0	259	287	284	281	294	247	287
	50	329	292	272	282	301	259	316
	100	282	298	311	317	313	265	325
	300	—	356	348	323	363	317	414
Q‡	0	1.45	1.44	1.43	1.44	1.44	1.45	1.48
	50	1.63	1.50	1.44	1.46	1.55	1.49	1.61
	100	1.55	1.50	1.68	1.62	1.65	1.51	1.58
	300	—	1.70	1.78	1.73	1.76	1.67	1.99
Vapor pressure osmometry results								
$\bar{M}_n$§ (approx.)	0	2410	2610	2630	2720	3390	2440	3072
$\bar{M}_n$¶	0	—	—	—	—	—	3490	—
	50	—	—	—	—	—	3730	—
	100	—	—	—	—	—	3680	—
	300	—	—	—	—	—	3200	—

* Number average chain length in angstroms
† Weight average chain length in angstroms
‡ $Q = \bar{A}_w/\bar{A}_n$
§ Number average molecular weight (one point determination) by VPO technique
¶ Number average molecular weight by VPO technique at $c = 0$

electron-degraded molecules from the film surface are mixed with bulk film material during repeated development/erase cycling so that homogeneous radiation damage to the material is considered the net result.

This conclusion is further supported by melt-viscosity data obtained for the polymers listed in Table 6. The effective shear rate during development is very low, and the experimentally observed viscosity cannot be related directly to the effective viscosity of the polymer during such development. These measurements therefore reflect changes in polymer properties that are assumed to cause parallel changes in response characteristics. Insufficient data exist to specifically test this assumed relationship. The curves of viscosity η vs. shear rate σ in Fig. 7 show a peculiar anomaly. In all cases a maximum is observed, the position and height of which depends on temperature (see Fig. 8), chemical structure, and dosage of gamma radiation. Such data show the ability of radiation to induce changes in molecular weight, molecular weight distribution, and polymer architecture. Such changes resemble the shear-rate dependence of viscosity at various temperatures.

Viscoelastic materials of high molecular weight normally have melt viscosities that decrease with shear rate, while polymers with low molecular weights can be expected to have shear-independent viscosities [2]. The co- and terpolymers investigated in this laboratory appear to undergo a type of ordering or gel formation as the shear rate is increased from zero until a maximum viscosity is reached. At higher shear rates, beyond the viscosity maximum, the apparent order is lost by decreasing with increasing shear. Since this phenomenon was not observed with either of the homopolymers [3], it is quite unlikely to be an experimental artifact and does indeed reflect an ordering that must result from an intermolecular force, possibly due to an interaction between unlike monomer units.

Examination of the radiation-induced changes in average molecular sizes and their distributions, obtained by

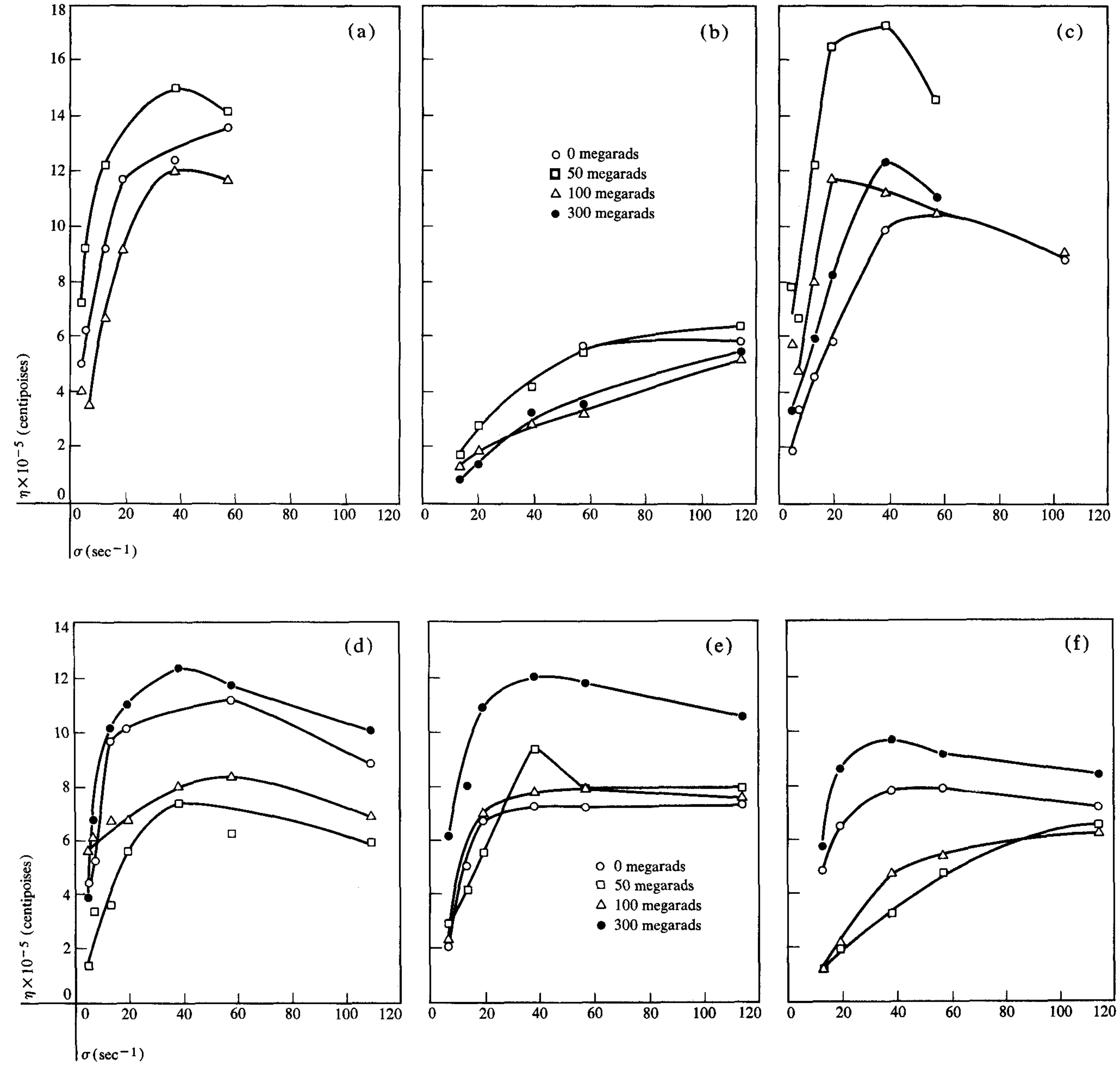


Figure 7 Melt viscosity vs shear rate. (a) Styrene-hexyl methacrylate (85–15 mole ratio) at 100° C. (b) Styrene-hexyl methacrylate (80–20 mole ratio) at 100° C. (c) Styrene-hexyl methacrylate (75–25 mole ratio) at 85° C. (d) Styrene-hexyl methacrylate-2-ethylhexyl acrylate (80–16–4 mole ratio). (e) Styrene-hexyl methacrylate-2-ethylhexyl acrylate (80–4–16 ratio) at 80° C. (f) Styrene-octyl-decyl methacrylate (80–20 mole ratio) at 80° C.

GPC and shear dependence of viscosity, shows the following. The 80-20 styrene-hexyl methacrylate copolymer resists radiation better than the 80-20 styrene-octyl-decyl methacrylate copolymer. Data on molecular sizes show that a better balance between concomitant and compensating cross-linking and scission effects is obtained with the copolymer containing hexyl methacrylate at the aforementioned level of internal plasticization, i.e., the net changes in molecular size are smaller, and the broadening of the distribution less pronounced. Such data are consistent with published results which support the view that the longer hydrocarbon tail leads to greater cross-linking [4].

The introduction of more hexyl methacrylate into the copolymer structure to increase the level of internal plasticization has the anticipated effect of altering the balance between radiation-induced cross-linking and scission. The 75-25 styrene-hexyl methacrylate copolymer apparently underwent more scission to produce an initial reduction in molecular size than did the analogous 80-20 copolymer. In addition, changes in molecular size and distribution during irradiation show that the protective effect of the styrene unit is lessened. The shear dependence of viscosity reflects the better radiation resistance of the 80-20 styrene-hexyl methacrylate copolymer; see Figs. 7(b) and (c).

Substituting a varying amount of 2-ethylhexyl acrylate (a cross-linking unit) for hexyl methacrylate in the parent copolymer structure results in radiation-induced changes that are difficult to explain. However, some conclusions can be drawn. The molecular size distribution becomes uniformly broader with increasing radiation exposure and 2-ethylhexyl acrylate content, but such changes are less than for styrene-octyl-decyl-methacrylate copolymers.

Gel-permeation-chromatographic and shear-dependent viscosity results obtained with these irradiated polymers show that significantly smaller changes in molecular size of the styrene-hexyl methacrylate-2 ethylhexyl acrylate terpolymers result in greater bulk viscosity changes than do similar molecular variations in the styrene-octyl-decyl methacrylate (80-20) copolymer. Such results emphasize that one must take great care in drawing conclusions about the viscosity-dependent response characteristics of thermoplastic materials from molecular weight (size) measurements alone. Although the bulk viscosity of polymers is intimately related to the molecular weight, radiation-induced changes produce such effects as grafting, unsaturation, distribution alteration, etc., which alter this relationship. Such configurational and distributional changes are known to have a significant effect on the flow properties of polymers.

- *Photoconductive terpolymers*

Electrostatic charge patterns produced by selective destruction of a uniform surface charge, and readout by electron beam, require a thermoplastic with special electrical properties. There should be sufficient dark resistivity to permit the application of a charge and subsequent thermal development, yet the material must be able to bleed off charge when subjected to radiation. Such requirements suggested the introduction of photoconductive units into the thermoplastic material. In order to avoid polymer incompatibilities and sublimation difficulties that might be associated with small molecules as photoconductive plasticizers, a number of polymers containing photoconductive structural segments were synthesized. These included a series of N-vinylcarbazole-styrene-octyl-decyl-methacrylate terpolymers ranging in compositions from 70-0-30 to 10-60-30 mole percent with replacement of the N-vinylcarbazole group by styrene in increments of 10 mole percent. The terpolymer of composition 60-10-30 did not deform in the dark on the in-air recording apparatus, probably because of both increased dark conductivity and increased glass transition temperature (hence an increased deformation temperature) resulting from the incorporation of the carbazole unit. The 50-20-30 terpolymer and all subsequent members of this series with lower N-vinylcarbazole contents did deform in the dark on the in-air recording device. However, the 50-20-30 polymer did not respond when subjected to electron-beam bombardment in the cycling apparatus. Apparently the more energetic electrons in the electron beam induced greater electrical conductivity than was observed with corona charging.

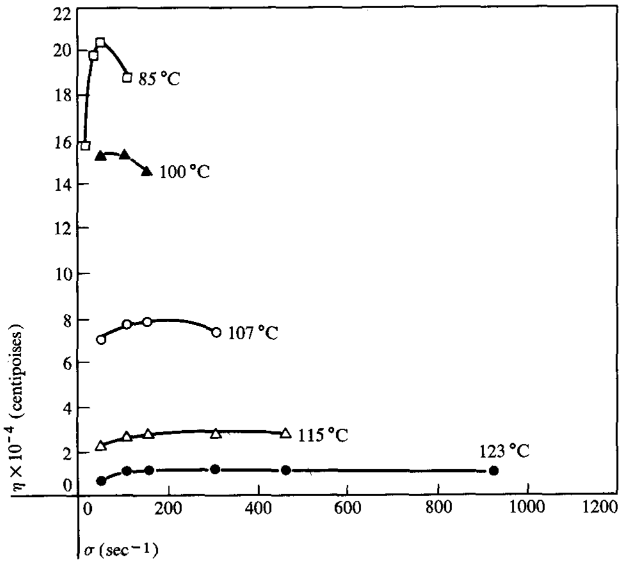


Figure 8 Melt viscosity vs. shear rate for styrene-hexyl methacrylate (75–25 mole ratio).

Such results clearly show that in thermoplastic recording, a priori specification of photoconductivity properties of a material cannot be made unless the device and charging system are specified. It is more expedient to prepare materials with a range of properties and then determine under realistic conditions the most appropriate composition.

A 40-30-30 terpolymer from this series of photoconductive terpolymers was cycled in the vacuum system previously described for a total of 11,500 cycles. The develop and erase temperatures changed from 55°C and 97°C respectively at 1000 cycles to 69° and 104°C at 11,500 cycles. Thus it appears possible to specifically tailor a macromolecular structure to provide responsive and reversible thermoplastics having photoconductive properties.

Summary

The experimental observations given in this paper provide a set of guidelines that relate molecular weight, degree and type of plasticization, and polymer chemistry to the thermoplastic recording properties of a polymer. During the course of this work, examples of responsive and highly reversible recording media were produced; these materials have been shown to be suitable for either corona- or electron-beam writing with either Schlieren optical or electron-beam readout.

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H. R. Anderson, Jr. is located at the IBM Systems Development Division Laboratory, San Jose, California 95114; E. A. Bartkus, at the IBM Systems Development Division Laboratory, Boulder, Colorado 80301. J. A. Reynolds is a member of the faculty at Duke University, Durham, North Carolina 27706.