Characteristics of Direct Current UV Lamps and
Their Effect on Curable Films

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It has been about 50 years since the printing industry was first introduced to UV-curable ink that "dries" in an instant when irradiated with UV light. During this time, the application of UV-curable materials has been extended to a variety of fields beyond printing with an evolution from the earliest materials (which targeted the goal of simple 'drying' by UV radiation) to functional materials offering greater added value. In particular, UV-curing technology is now being used for producing a variety of optical films for flat panel displays (FPDs) as well as optical recording media such as CDs and DVDs, leading to an even wider appreciation of the importance of this technology.

The diversification of fields using materials displaying functional properties conferred by the microstructure formed through the UV-curing reaction has been accompanied by a renewed awareness of UV-emitting light sources, which have previously received little attention. The UV-curing process determines the final properties of the UV-curable material, but the source which emits UV light is not merely a light-emitting device. The emission behavior of the light source also has a significant influence on the crosslinked microstructure, playing a crucial role in altering, potentially to a great extent, the final properties displayed by the cured material.

The UV-curing reaction produces a 3-D crosslink through photoinitiated polymerization with crosslinked networks being formed through propagation reactions beginning at initiation points (radical generation points). According to Kloosterboer *et al.*,[1-4] in the first stage of polymerization, microgels are generated from the polymerization initiation point, and with time these develop into macrogels. These macrogels are further combined in a termination reaction, forming a structure having large crosslinks. UV-cured materials, therefore, have a microstructure that is inhomogeneous around the initiation points. This microstructure can be changed considerably, depending on the generation state of the initiating active species propagated as a result of UV irradiation. This inhomogeneity is the most significant characteristic of the crosslinked structures obtained from UV-curing reaction, differentiating them from homogenous crosslinked structures produced as a result of thermal-curing reactions. Figure 1 shows an abstract representation of a

crosslinked structure formed as a result of the UV-curing reaction.

In this article, the light emission behavior of UV-emitting light sources will be shown and how they greatly depend on the power source current. It will also describe how these differences in the light emission behavior of light sources influences the efficiency of the UV-curing reaction and the microstructure of the cured material.[5] Factors contributing to these differences will

FIGURE 1

Abstract representation of crosslinking reaction (UV-curing reaction)

(a)

Generation of microgels from polymerization initiation points

(b)

Growth from microgel into macrogel

(c)

Formation of crosslinked structure (cured material)

also be examined with an analysis of the UV-curing reaction mechanism in terms of polymerization kinetics.

### Electrode Lamp Experiments

The alternating current, like the one shown in Figure 2, is a familiar means for igniting electrode lamps, which utilize arc discharge from a filament. In order to investigate the effect of the lamp's supply current on emission behavior, ignition tests were conducted on an electrode lamp connected to a fully rectified direct current supply. The emission profile of the lamp when ignited by AC and also DC power supplies were measured by passing a photometer (EIT UV Power Map, sampling at 2,048 Hz) beneath the lamp. The same lamp was used in both tests. Figure 3 shows emission profiles produced by each power supply and an expanded view of the time axis at the point where the respective profiles overlap.[6] It is clear from these graphs that the DC lamp emitted light smoothly over time with no sharp fluctuations in intensity. Such light emission is known as "constant light." In contrast, the emission profile of the conventional electrode lamp displays waves or ripples

over time, resembling a pulsated emission behavior. Their emission intervals are about 8.3 milliseconds and correspond to the alternating current cycle (emission using 60 Hz supply). Alternating current cycle is 50 Hz in eastern Japan and 60 Hz in western Japan.

In order to understand how this difference in emission behavior affects the UV-curing reaction, the reaction conversion of an isobornyl acrylate system, which was supplemented with Ciba IRGACURE 184, was measured by UV irradiation, then using FTIR to determine the amount of residual double bonds. Figure 4 shows the change in conversion relative to conveyor speed in both nitrogen and atmospheric gas.[5] This graph shows that under all irradiation conditions a higher conversion was achieved with irradiation by the DC light source than by the AC light source. Using the conversion obtained from the DC light source as a baseline, the differential between this baseline and the conversion obtained from the AC light source was plotted against the conveyer speed (Figure 5). It is clear from this graph that, under both nitrogen and atmospheric gas,
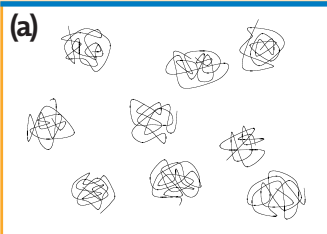
FIGURE 2

Alternating current (AC) and direct current (DC)

Alternating Current   50Hz or 60Hz

AC

Direct Current

DC
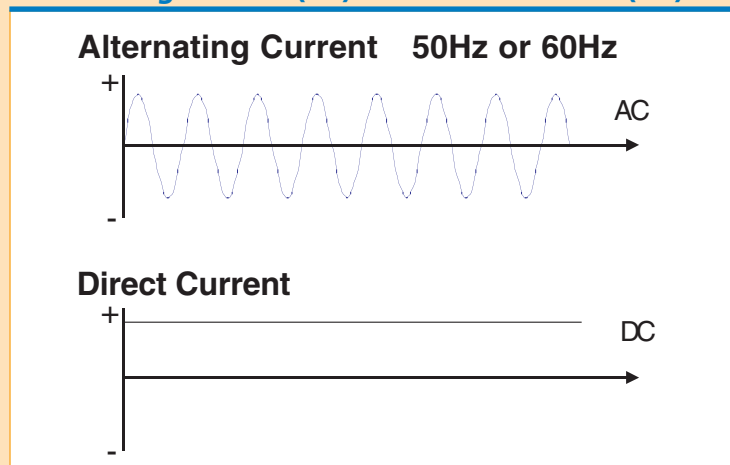
the conversion differential due to differences in light source emission behavior widens as conveyor speed increases. The graph also shows that this conversion differential is greater in the nitrogen gas environment, in which the radicals that form the active polymerization species are longer lived. These results indicate that the emission profile of the UV-irradiating light source has a considerable impact on the reaction conversion in UV-curing reactions.

Emission Profiles and Reaction Conversion of Electrodeless Lamps

Unlike electrode lamps, the electrodeless lamp does not emit light through arc discharge between electrodes, but rather through the generation of microwaves (electric waves) by a magnetron. Although the magnetron is powered by direct current, UV radiation devices that are currently available commercially adopt two kinds of rectification. The first

type (Figure 6) is known as full-wave rectification and rectifies by reversing one half of the alternating current waveform. The second type is converted to a complete direct current. The emission profiles of these two types of UV irradiation devices were measured in the same way as the electrode lamp profiles described above. Figure 7 shows an irradiation device ignited by a full-wave rectified direct current. The emission profile displays ripples due to the effect of the rectified waveform. This graph was obtained with a 50 Hz rectified current, having emission peaks at 10 millisecond intervals. In contrast, the lamp ignited by the complete direct current was found to generate a perfect constant light free of this ripple effect.

The conversion of isobornyl acrylate under these two types of light sources was measured in the same way as for the electrode lamps. The results obtained under irradiation at a conveyer speed of 45 m/min are shown in Figure 4b. These results show that, as with the electrode lamps, the highest reaction conversion value was achieved under irradiation from constant light. The reaction conversion under the electrodeless lamps was higher than the value obtained under the electrode lamps at the same conveyor speed because of the higher intensity (photon density) of the electrodeless lamp.

Factors Contributing to Conversion Differential

In this section, why UV irradiation source emission profiles influence reaction conversion during the UV-curing reaction will be contemplated. As stated above, the UV-curing reaction creates a 3-D crosslink through photoinitiated polymerization. Each of the polymerization elementary reaction is shown in the reaction schemes described.

FIGURE 3

Emission profile of an electrode lamp
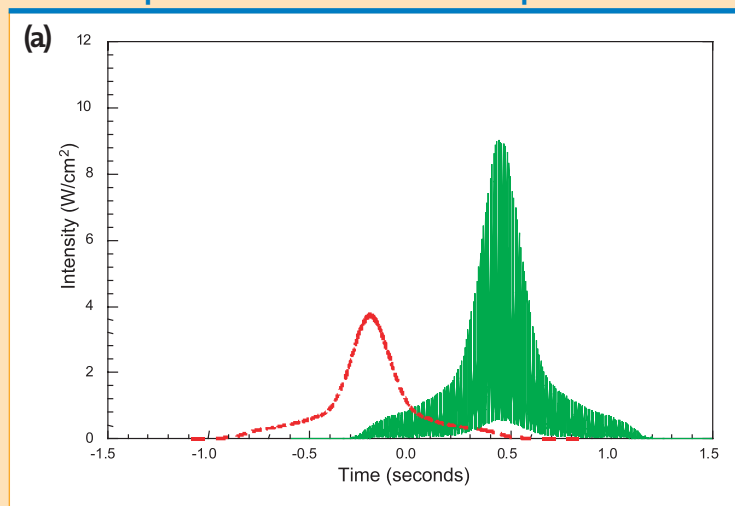
Emission profile obtained from an electrode lamp ignited by alternating current (-) and direct current (—)
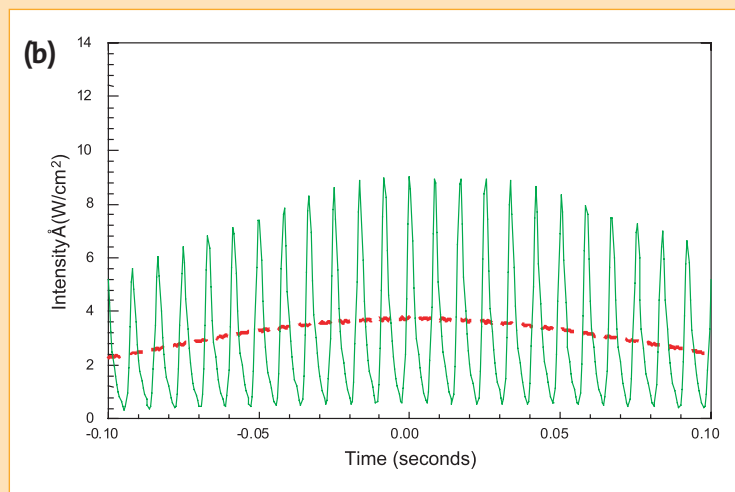
Expanded view of (a). The AC emission profile contains 12 peaks in each 0.1 second interval (measured at 60 Hz)

1) **Initiation reaction**
   [photochemical process]
   l→l*→R · Generation of
   polymerization initiation radical
   (electron excitation state)

   [dark polymerization process]
   R · + M→RM · Initiation reaction

2) **Propagation reaction**
   $$k_p$$
   $RM_n · +M→RM_{n+1}$

   k_p: propagation rate constant

3) **Termination reaction**
   k_t
   $M_m · +M_n→M_{m+n}$ (recombination)

   k_t: termination rate constant

As this photoinitiation polymerization scheme shows, the contribution of UV light is limited to the nascent stage of the initiation reaction, the stage in which electrons in the initiator molecules enter a state of excitation. On absorbing UV light, the initiator molecules are excited into an excited singlet or excited triplet state, producing intramolecular cleavage or hydrogen abstraction reactions. Thus, generating ground state radicals, which are the active species in polymerization initiation. These electron excitation states last in the order of nanoseconds for excited singlet state and microseconds for the excited triplet state at room temperature. However, as described, in irradiation by UV devices producing a ripple pattern, the emission intervals are in the order of millisecond and, therefore, the short-lived nature of the electron excitation state means that there will be timebands in which UV irradiation is too brief and no active initiation species are produced. In other words, under ripple-type irradiation, there are timebands in which only propagation and termination reactions

FIGURE 4

Photopolymerization conversion of isobolnyl acrylate

(a)

Conversion within N2 atmosphere to which 0.25% Ciba IRGACURE 184 was added

(b)
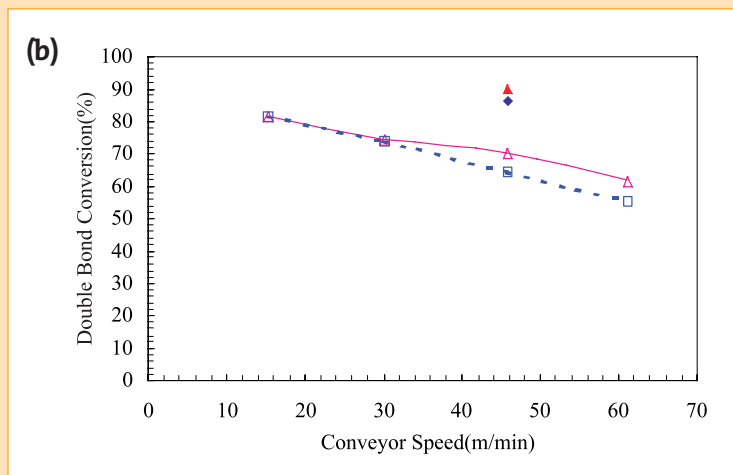
Conversion in atmospheric gas to which 2% Ciba IRGACURE 184 was added
□ : Irradiation by AC ignited electrode lamp
Δ: Irradiation by DC ignited electrode lamp

occur, and timebands in which a 'constant state' of equal initiation and termination rates is not established.

Based on the above reaction formula described, the polymerization propagation rate R_p is:
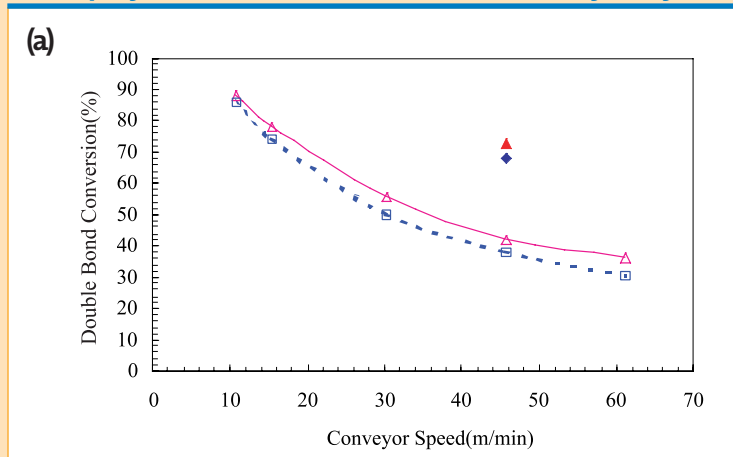
$R_p = (k_p/k_t^{1/2})(\_l_a[l]^{1/2})[M]$ (Formula 1)

In this formula, k_p is the propagation rate constant and k_t is the termination rate constant, _ is the quantum yield of radical generation in the initiator, l_a is the quanta of light absorbed by the initiator, [l] is the concentration of the

initiator, and [M] is the concentration of monomer (concentration of double bonds).

In the photoinitiated polymerization of isobornyl acrylate described, the $(\_l_a[l]^{1/2})[M]$ term of Formula 1 is the same for both constant-light irradiation and ripple-light irradiation. Therefore, the main cause of the conversion difference can be expected to reside in the values for $(k_p/k_t^{1/2})$, which differ depending on the irradiation device. However, because the value for k_p is

FIGURE 5

Conversion differentials between irradiation under DC and AC electrodeless lamps (-_- in N$_2$; - _ - in Air)
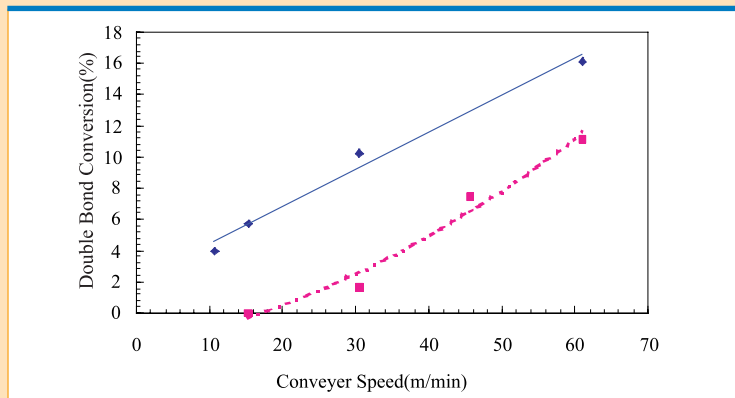
As the irradiation increases, the conversion differential becomes magnified. The conversion differential is immense within N2, which radicals are longer lived.

the value for isobornyl acrylate, therefore the same in both cases, the conversion differential arising from the different emission profiles of the two different light source types must be attributed to the different k_t values. In other words, it would appear that the termination reaction occurs earlier under pulsated ripple irradiation than under the constant irradiation produced by a direct current.

Under constant light irradiation, the main termination process is a termination reaction predicated on recombination of 'normal' propagating radicals, but (as described above) under ripple irradiation, there exists a timeband over which only the active reaction species exists as the propagating radical. This leads to an increase in the proportion of termination reactions other than termination by recombination of 'normal' propagating radicals. In such a polymerization system, after production of a propagating radical, a low-molecular weight radical (e.g. initiator radical) is newly produced by the intermittently irradiating light and recombined preferentially with

the propagating radical end-group to terminate polymerization. In other words, because the low molecular weight radicals continually produced by intermittent UV irradiation are highly mobile and diffuse easily, they become prematurely recombined with the propagating polymer radical

end-groups, thus terminating polymerization early.[7,8] This is why the ripple irradiation system shows a higher kt and lower R_p value than does the constant irradiation system, and this difference in R_p values can be seen to manifest as conversion differential between the two irradiation systems. A schematic representation of the two different types of termination reaction is shown in Figure 8.

M = Monomer; R. = low-molecular weight radical (including initiator radicals)

As was shown in Figure 1 at the onset, UV curing brings about the formation of an inhomogeneous crosslinked structure, but at the initial stage of irradiation a greater amount of microgel is formed under ripple irradiation than under constant irradiation. In order to visually inspect this condition, a curable film of trimethylol propane triacrylate (TMPTA) was examined at an early stage of curing by phase contrast microscope. Because UV

FIGURE 6

Full-wave rectification and complete direct current rectification
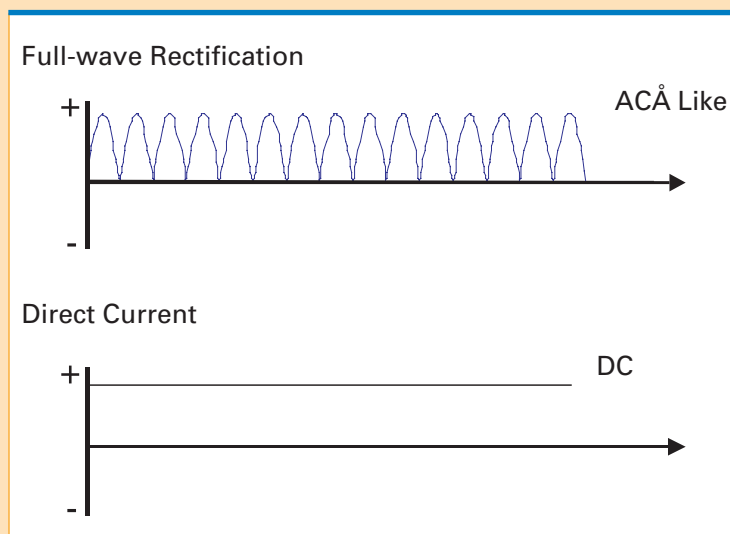
irradiation eliminates the double bonds of the TMPTA acryl group, therefore altering the material's refractive index, it is possible, by using the phase contrast microscope, to directly observe the refractive index differential vis-à-vis the UV irradiation medium.

Figure 9 shows phase contrast micrograms of transparent cured TMPTA films (thickness: approximately 100 µm) obtained by UV irradiation from an electrode lamp, a full-wave rectification electrodeless lamp and a direct current electrodeless lamp. In these photographs, dark and light patches indicative of domain formation are clearly visible in the cured films irradiated with the electrode lamp and the full-wave rectification electrodeless lamp, both of which produce ripple-type emissions. Under the electrodeless lamps, which have higher intensity, the contrast is higher and the domain structure (phase separated structure) is more clearly visible. In contrast, under the direct current electrodeless lamp, this type of macro-domain structure was not observed, indicating that there was no domain formation under this type of lamp, at least at the scale observable by optical microscopy. The premature termination reaction described above occurs more readily under ripple irradiation than under constant irradiation, and it is this which is thought to lead to the formation of the kind of large domain structures seen in the photographs.

Conclusion

The nature of the UV-curing reaction means that it produces an inhomogeneous crosslinked structure, but the choice of irradiation source has been shown to have a considerable impact on the curing conversion rate and the micro-domain

FIGURE 7

Emission profiles of electrodeless lamps

Emission profile for full-wave rectification, ripples are present, with 10 peaks in each 0.1-second interval (measurement at 50 Hz)

Emission profile for complete direct current

structure of the cured material. Until now the nature and properties of the light emitted from the UV-irradiation source have been a somewhat overlooked aspect of the UV-curing reaction, but this situation is changing. The fields of application of UV-curing technology are growing and is now being used in the field of high-performance materials, which display properties closely linked to the microstructure of the cured material. By using UV-irradiation devices powered by direct current, it is now possible to achieve constant light irradiation and thus reduce premature
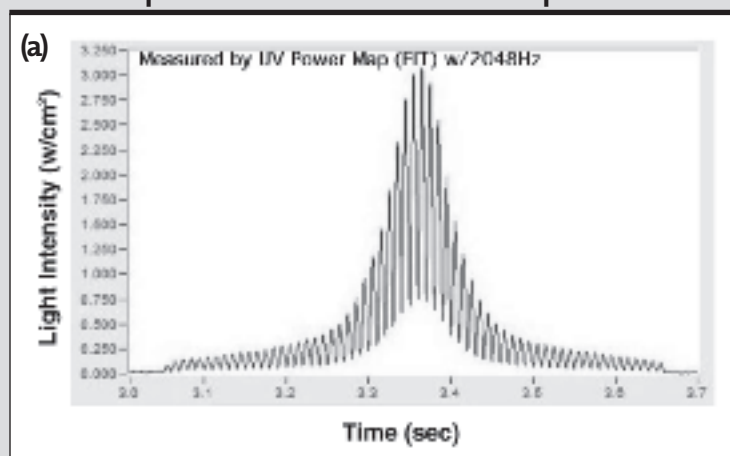
termination reactions in the UV-curing reaction. It is likely that UV-curing technology will continue to be used in fields for developing new high-performance materials and, as for the UV-irradiation source itself, one can expect to see the direct current lamp making a large contribution within these fields.
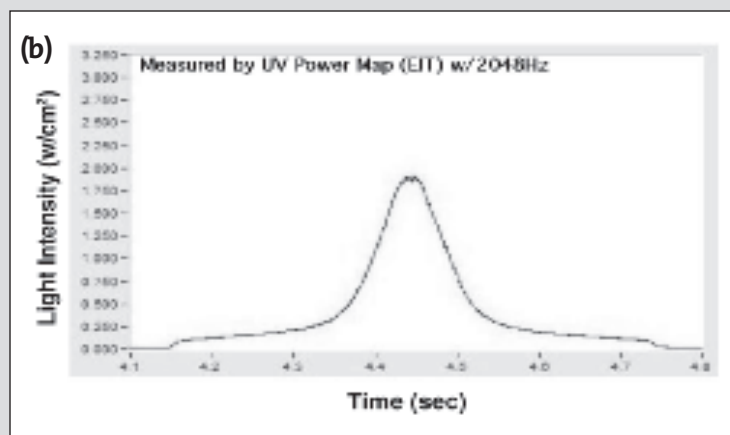
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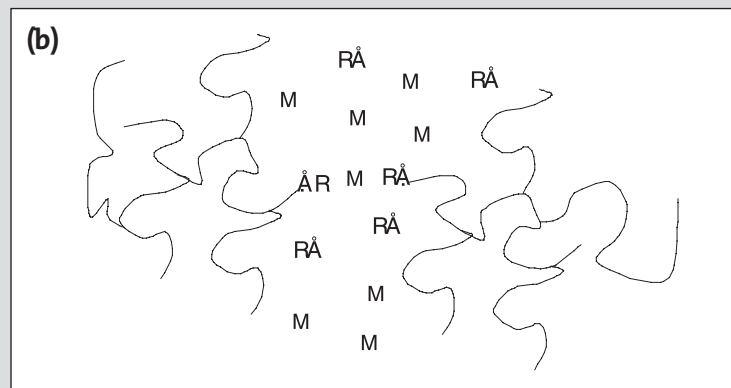
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FIGURE 8

Schematic representation of termination reaction by radical recombination
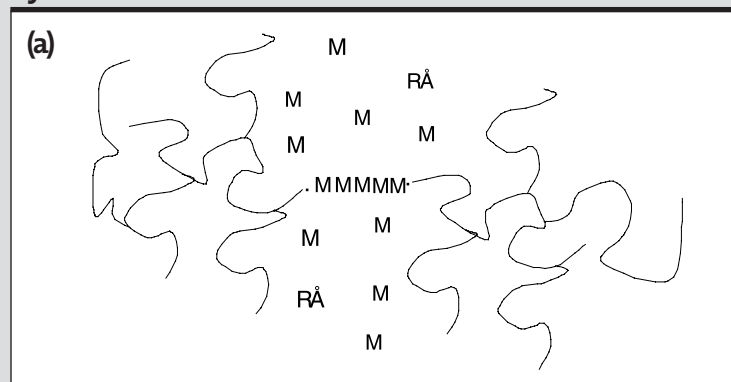
Recombination by "normal" end-group propagating radicals

Premature termination reaction by low-molecular weight radicals produced by intermittent UV irradiation

FIGURE 9

Phase contrast micrographs of cured film of TMPTA supplemented with 1% Ciba Irgacure 184 (optically inhomogeneous curing domains are visible, formed by ripple-type irradiations in electrode and full-wave rectified lamps)

(a) *Electrode lamp*

(b) *Full-wave rectified electrodeless lamp*

(c) *DC electrodeless lamp*